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# RESEARCH
# ON CRYSTALLINE SYNTHETIC HIGH POLYMERS WITH A STERICALLY REGULAR STRUCTURE

ISTITUTO DI CHIMICA INDUSTRIALE DEL POLITECNICO DI MILANO

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SUPPLEMENTO AL VOLUME XV, SERIE X
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N. 1, 1960
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# Crystalline Synthetic High Polymers with a Sterically Regular Structure.

## Introduction.

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(ricevuto il 7 Agosto 1959)

The discovery of stereospecific polymerization processes leading to new linear high polymers of vinylic and diolefinic hydrocarbons having a regular structure, also with regard to the steric configuration of the monomeric units, probably represents the most important event in the pure and applied macromolecular chemistry, during these last 20 years.

Even if it is a fairly recent discovery (the first patents on the subject were filed in June 1954 [1] and the first scientific communication was presented in December 1954 [2] before the Accademia dei Lincei) nevertheless its influence was considerable and roused a wide international movement of researches, to which thousands of chemists devoted themselves in university and industrial research laboratories. These researches brought to the discovery of a great number of new stereo-ordered polymers.

The new processes are important because with the old processes a great number of simple monomers, able to give asymmetric monomeric units by polymerization, could only be polymerized to products having an irregular structure due to the random distribution along the chain of isomeric monomeric units with different steric configurations. As a result of chemical and steric structure irregularities, the macromolecules presented in the solid state lack of crystallinity and of suitable mechanical properties and therefore there were only a few possibilities of valuable applications [3].

Even before the discovery of the stereospecific polymerization processes, different types of synthetic and natural macromolecules with sterically regular structures were known. Some of these macromolecules are thoroughly related to many phenomena of the organic life.

In the field of linear macromolecules, some crystalline natural products (*i.e.* cellulose, silk, etc.) show sterically regular structures, because they contain asymmetric carbon atoms, but only one of the two possible enantiomorphous forms is present. Thus the steric structure regularity of those polymers is due to a regularity already existing in the monomers which contain asymmetric carbon atoms. The monomers of those natural products exhibit an optical activity; in fact they rotate the plane of the polarized light; therefore the steric regularity of the corresponding polymers is not determined by the polymerization process which does not modify the steric structure of the monomeric units.

The new stereospecific polymerization processes recently discovered give the possibility of obtaining sterically regular polymers (which contain asymmetric carbon atoms) also starting from monomers which, actually, do not have asymmetric carbon atoms, owing to the fact that the asymmetric carbon atoms are formed only during the polymerization reaction. They give the possibility of realizing a synthesis which can be defined as asymmetric in respect to the monomeric units of a single macromolecule with a sterically regular structure [3]. The crystallizability of the macromolecules of this kind is due to the presence, at least for long sections of the main chain, of asymmetric carbon atoms having the same steric configuration.

Other examples of natural polymers with steric regularity (which imply the so-called geometrical asymmetries and not the optical ones) are given by natural rubber and guttapercha, both being isoprene polymers with 1-4 enchainment: the former being almost completely (~ 97 %) formed of cis units, the latter of trans ones. The poor elastic properties of all synthetic rubbers known before 1954 in comparison with natural rubber, depended on the reason that the chemists were then unable to produce diolefin polymers having a high steric purity due to cis 1-4 enchainment.

The new processes of stereospecific synthesis allowed the U.S. chemists to produce a sterically regular cis 1-4 isoprene polymer very similar to natural rubber [4] and the Italian ones to synthesize for the first time the trans 1-4 polyisoprene [5] and all the stereoisomer polymers [6] (isotactic 1-2, syndiotactic 1-2, trans 1-4, cis 1-4) of butadiene (a diolefin less expensive than isoprene). The synthetic rubbers produced with these processes, having cis 1-4 enchainment and a very high steric purity, have, as natural rubber, high elasticity, low hysteresis and high tensile strength also in vulcanizates without reinforcing fillers [7].

Physico-chemical methods (in particular the interpretation of the X-ray and electron diffraction and of the I.R. spectra) mostly contributed to the discovery of the new stereoregular polymers and to their characterization; they also helped to determine the inward structure of the polymeric chains and of their crystalline aggregates, to distinguish polymers with different types of enchainment and of steric order, and to determine the degree of steric purity.

On the specific results in the field of cristallinity obtained by these methods we have published only preliminary works till now, which were sufficient to recognize and distinguish the new types of macromolecules. We did not publish the whole set of works because we were to devote most of our time to the study of catalysts, of the polymerization processes and of the other properties of the new polymers. Just recently we had the possibility of reorganizing the various experimental works we collected during these years of researches.

I therefore accepted the kind proposal of Prof. POLVANI who, last year, invited me to publish some significant parts of our researches in the macromolecular field in this Journal, limiting them to the above-mentioned field of the polymeric structures in the crystalline state.

Considering the character of this review, I do not describe the nature and mechanism of the chemical processes of stereospecific polymerization developed to synthesize linear head-to-tail polymers, where monomeric units with a certain type of steric structure are orderly disposed. At the end of this issue we report the bibliographies of a great number of papers concerning the chemical processes of polymerization carried out at the Polytechnic of Milan. This introduction is followed by ten notes: in the first note are described our original observations, on the principles determining the chain conformation of the linear high polymers in crystals. We proved the remarkable usefulness of these principles to interpret the structures of the new isotactic polymers and, recently, also to determine the structure of syndiotactic alpha-olefin polymers and of the di-isotactic ones we synthesized. The crystalline structure of some stereo-ordered polymers is described in the following 7 notes. The two last notes on I.R. spectroscopy complete the study of crystallinity with methods which are more suitable and sensitive than X-ray methods for the determination of limited degrees of order.

To make the reader realize the importance, in the macromolecular field, of crystallinity which depends on the regularity of the chemical and steric structure of the polymers I shortly summarize the difference in the mechanical properties which can be observed among the stereo-ordered polymers in comparison with those having a complete or partial steric disorder.

In the field of alpha-olefins, which are remarkably important because of the low cost of monomers (some of them are by-products of the petroleum industry), two types of steric orders are possible: the « *isotactic* » and the « *syndiotactic* » ones.

The isotactic structure of polymers is characterized by the fact that monomeric units (which may exist in two enantiomorphous forms, which cannot be superposed, one being the mirror image of the other) follow each other in the chain, at least for long chain sections, with the same steric configuration [8]. In the syndiotactic structure of polymers, on the contrary, a different type of order can be observed, owing to the fact that enantiomorphous monomeric units follow each other alternately [9]. Fig. 1 shows the chains of the isotactic [10] and of the syndiotactic polypropylene recently obtained in its crystalline state [11].

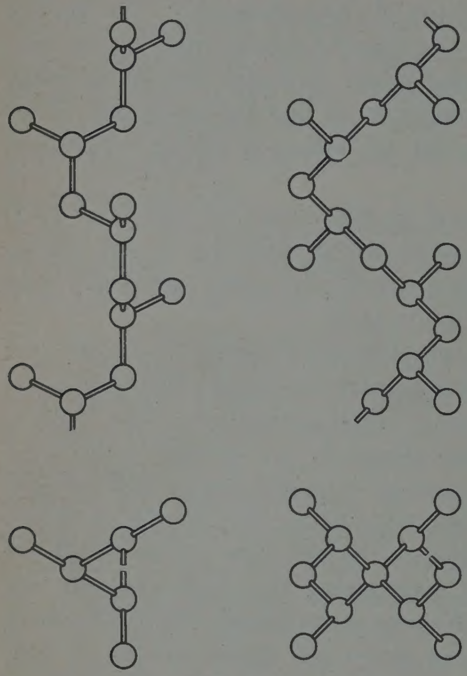

Fig. 1. – Conformations found in the crystals for the chains of isotactic (left) and syndiotactic (right) polypropylenes.

For the atactic polymers there is no order in the succession of the enantiomorphous monomeric units, and this is the reason for the lack of cristallinity.

Properties, which are very different from those of the stereoordered macromolecules (isotactic or syndiotactic) and from those of the sterically disordered atactic macromolecules, are shown by products with a degree of an intermediate order, which allows just a very little part of the polymeric chains to crystallize.

We called «stereoblock», the polymers formed of chain sections of different steric composition, which present a low degree of crystallinity [12].

As examples, we report some properties of high molecular weight (> 50 000) linear polypropylenes of different steric composition. The isotactic sterically pure polymers have a melting point of about 175 °C; in the non-oriented state they can be interesting as thermoplastic materials with elastic moduli (150 ÷ 200) kg/mm², maximum tensile strength by traction of about 4 kg/mm² and ultimate elongation of (400 ÷ 700)%. In the oriented state they furnish transparent films with a resistance to tensile stress in two orthogonal directions of about 20 kg/mm².

Oriented fibres exhibit elastic moduli of (300 ÷ 360) kg/mm² and resistance to tensile stress of (60 ÷ 70) kg/mm². Their lightness (density of 0.91 instead of 1.50 of cotton and of 1.14 of nylon), excellent mechanical characteristics, low cost, and high insulating properties, are strong arguments to consider these products as some of the most interesting in the field of synthetic textile fibres [13].

Atactic polypropylenes, on the contrary, are amorphous; if they are subjected to protracted stresses, they show high viscous creeps; in the vulcanized state they behave as elastomers. The inconvenience of the high elastic hysteresis of atactic polypropylenes can be reduced, introducing, as we did, by copolymerization, more flexible ethylene monomeric units in the polypropylene chain; as a result, the amorphous ethylene-propylene copolymers represent interesting synthetic rubbers, which are cheaper and more ageing-resisting than natural rubber [14].

The influence which crystallinity exerts on the properties of diolefin polymers is very important. As regards butadiene stereo-ordered polymers, isotactic and syndiotactic polymers with 1-2 enchainment, are crystalline and have high melting temperatures (respectively 125 °C, 155 °C). They are hard materials with a high elastic modulus and they are thermoplastic if cross-linking is absent.

The corresponding atactic polymer is a rubber which shows high elastic elongations, low moduli and relatively high elastic hysteresis because the presence of vinyl side groups introduces a certain hindrance to the free rotation of the C—C bonds of the main chains.

The polymers with 1-4 enchainment have been prepared in two sterically ordered forms: cis [5] and trans [6] respectively. The trans form of polybutadiene has a high melting temperature (148 °C) and only if crystallinity is hindered either by an increase of temperature or by different systems of plasticization or by vulcanization, it behaves as an elastomer: it gives hard rubber-like products having a fairly high elastic modulus.

The cis 1-4 polybutadienes with a high steric purity crystallize at room temperature under stretching (as natural rubber and cis 1-4 synthetic polyisoprene), while the previously known synthetic rubbers did not crystallize. The initial elastic modulus is low, but crystallinity, produced by the orientation of macromolecules because of stretching, causes an increase of the elastic modulus, with the increase of the elastic deformation, and furthermore gives a very high value of the ultimate tensile stress [15].

Contrary to natural rubber, sterically pure cis 1-4 polybutadiene shows low hysteresis even at very low temperatures, and high resistance to abrasion.

The technological information we give in this short introduction, has been reported with the purpose of pointing out the importance of the steric order on crystallinity and on the mechanical properties, and in particular on the elastic properties of the new polymers. Fuller details are reported in the original works. They can make anybody realize the enormous interest which was introduced by the discovery of stereospecific polymerization processes in the field of plastics, of synthetic fibres and of elastic rubbers.

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# General Considerations on the Structure of Crystalline Polyhydrocarbons (*).

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(ricevuto il 26 Giugno 1959)

Owing to the discovery of stereospecific polymerization processes effected in our Institute, we were able to determine, in the last few years, the crystal structure of a great number of new polymers. In this work we will discuss the general principles, leading to the determination of the shape and mode of packing of macromolecules in the crystals [1].

## 1. – Stereoisomerism in head-to-tail aliphatic linear polymers.

Before explaining the principles and discussing, in accordance with them, the crystal structure of some macromolecular compounds, we would like to emphasize the importance of stereoisomeric phenomena in order to determine the ability of the polymers to crystallize.

There are different types of stereoisomerism in organic chemistry, generally distinguished into two classes:

1) geometrical stereoisomerism, whenever the same chemical formula may correspond to intrinsecally different geometrical configurations (*e.g.*, in compounds containing a double bond, or in cyclic saturated compounds);

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(*) A preliminary communication on this subject has been presented at the meeting of the A.C.S. (S. Francisco, April 1958).

2) optical stereoisomerism, whenever a molecule cannot assume, by not prohibited rotations around single bonds, the enantiomorphous configuration (this is in most cases due to the presence of carbon atoms linked to four different substituents [2]).

These two cases are both important in macromolecular chemistry.

Since the definition of crystal implies a three-dimensional order, in order that a polymer be crystallizable, a regularity in the succession of configurations of its monomeric units is necessarily required. A crystalline polymer can be obtained, in fact, only when all monomeric units belonging to a long chain segment show the same configuration, or when enantiomorphous configurations follow each other orderly. On the contrary, amorphous polymers are obtained when different stereoisomeric configurations of the same monomeric unit, *e.g.* cis and trans, or those « left » and «right» handed, follow each other disorderly. The stereospecific polymerization processes, first carried out in our Institute, permitted us to obtain head-to-tail linear polymers of alpha-olefins and di-olefins arranged according to regular successions of monomeric units, having equivalent steric configurations. These polymers are, generally, characterized by a high degree of crystallinity.

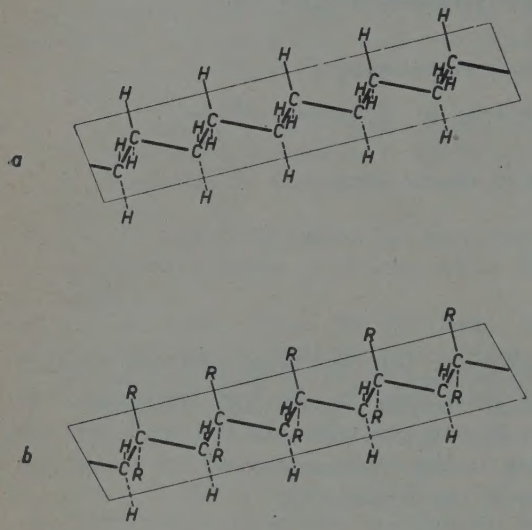

Fig. 1. – A head-to-tail succession of (*a*) ethylenic (—$CH_2$—$CH_2$—) or (*b*) vinylidenic (—$CH_2$—$CR_2$—) monomeric units may be realized in one way only (main chain arbitrarily stretched on a plane).

Before their discovery only a relatively limited number of crystalline synthetic hydrocarbon polymers were known.

Those obtained by poly-addition generally derived from monomers, such as ethylene or some vinylidenic monomers containing at least two symmetry planes in their molecules (isobutylene, vinylidenechloride).

When these symmetrical molecules undergo a polymerization process, only one type of head-to-tail enchainment may occur, as shown in Fig. 1. On the contrary, alpha-olefins and di-olefins may give rise to various types of stereoisomeric modes of enchainment; actually all synthetic polymers of alpha-olefins and di-olefins, prepared before the discovery of stereospecific catalysis, were amorphous. Fig. 2 shows molecules of stereoisomeric vinyl polymers with the chain arbitrarily settled on a plane; the isotactic [3] polymers in which successive head-to-tail monomeric units show the same steric configuration; syndiotactic polymers [4], in which successive head-to-tail monomeric units show alternatively opposite steric configurations; atactic polymers in which successive head-to-tail monomeric units, having different configurations, are randomly distributed along the chain.

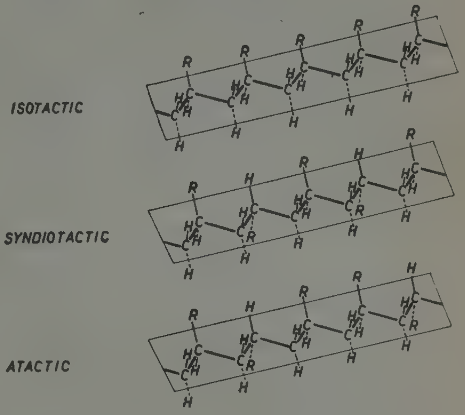

Fig. 2. – Various types of possible head-to-tail successions of vinylic (—$CH_2CHR$—) monomeric units: isotactic, syndiotactic, atactic (random); (main chain arbitrarily stretched on a plane).

In the field of di-olefin polymers other stereoisomeric phenomena of geometrical type appear: polyisoprene regular stereoisomers with 1,4 enchainment occur in nature; natural rubber has nearly a complete cis structure(~ 97 %), guttapercha has a trans structure. Other new stereoisomers of diolefins with 1, 2 enchainment, which do not exist in nature, have been synthesized in our Laboratory in the last five years.

The configurations of the four possible regular stereoisomers of polybutadiene, whose structure was studied by us, are shown in Fig. 3 [5]. Stereoisomeric phenomena are practically interesting in the field of polymers, since the most interesting physical and technological properties of isotactic polymers of alpha-olefins and of some new stereoisomers of polydiolefins, in the field of plastic materials and textile fibers, are due to the ability of crystallizing of these polymers [6]. Atactic polymers of alpha-olefins cannot crystallize and possess completely different properties. Their practical interest is confined to products with very high molecular weight, which give a particular type of elastomers.

The most characteristic features connected with crystallinity, such as the conformation of the chain in the crystalline state, the relative positions of the chains in the crystal, the degree of freedom of rotation of lateral groups, the rate of crystallization, the size, the distribution and the orientation of the crystals and so on, determine the most interesting technical characteristics of these polymers, *i.e.* hardness, mechanical properties such as modulus, ultimate tensile strength and elasticity, melting temperature range, molding properties and the possibility of giving high tenacity fibers.

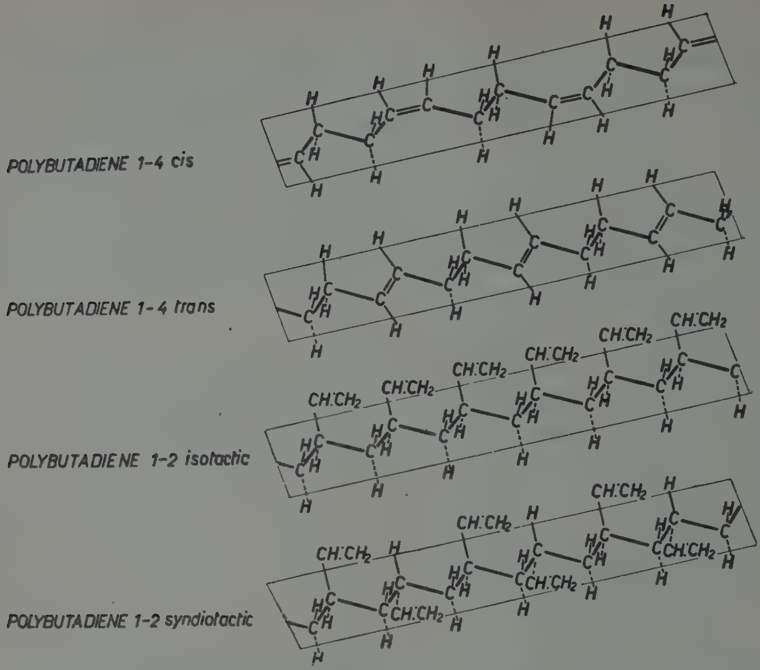

Fig. 3. – Regular successions of stereoisomeric butadiene monomeric units: cis 1-4, trans 1-4, isotactic 1-2, syndiotactic 1-2 (main chain arbitrarily stretched on a plane).

In this paper we shall examine the conditions to which the polymer is subjected to be crystallizable and the shape and mode of packing it will realize in the crystalline state.

## 2. – Shape and mode of packing of macromolecular chains in the crystals.

Regularity in the succession of monomeric units is the first requisite, as we have already seen, for a linear polymer to be crystallizable. As the definition of crystal implies three-dimensional order, a possible lack of order along the chain prevents in general any possibility of crystallization. It is actually observed that:

1) In linear crystalline polymers the axis of the macromolecule runs parallel to a crystallographic axis of the crystal. Moreover, in all known structures all the monomeric units have been found to occupy geometrically equivalent positions with regard to this axis (*) (*equivalence postulate*).

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(*) This is a sufficient, but not a necessary condition, to ensure order along the chain. Because this condition appears to be most frequently verified, it may be taken as a work postulate.

2) The conformation of the chain in a crystal approaches the one of minimum potential energy, that should be assumed by an *isolated* chain oriented along an axis, with the restrictions contained in the equivalence postulate. This means that lateral packing contacts (between neighbouring chains) generally play a secondary role in determining the conformation of the chain in comparison with the contacts internal in the chain. Thus, lateral packing contacts cause only slight deviations of the form of the chain from the one foreseeable only on the basis of the above considerations.

3) The chains approach themselves parallel each other at intermolecular distances similar to those realized in low molecular weight compounds, to fill possibly any hole between themselves. With this restriction, as many as possible elements of symmetry of the isolated chain are maintained in the lattice. That is, equivalent atoms of different monomeric units along an axis tend to assume equivalent positions in regard to the atoms of neighbouring chains.

Let us discuss orderly the bearing of these statements in the crystal structure of polymers.

**2·1.** *Equivalence postulate.* – According to the equivalence postulate, all the monomeric units which form a macromolecular chain occupy equivalent positions along an axis in the crystalline state.

In turn, a condition to be fulfilled by a crystallizable polymer, is that its monomeric units have configurations, as required in order that they may occupy equivalent positions along an axis. Let us call *isoclined* two monomeric units, whose equivalent atoms have the same $z$ co-ordinates after a suitable translation of the origin along the chain axis $z$; *anticlined*, two monomeric units whose equivalent atoms have the same $z$ co-ordinates after a suitable translation of the origin accompanied by a reversal of direction of the $z$-axis.

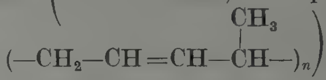
Repetition of equivalent monomeric units may be obtained along an axis in the following ways:

1) Repetition of isoclined isomorphous equivalent units: through the operation of a translation $c/p$ along $z$, accompanied by a rotation $2\pi(P/p)$ in a plane perpendicular to $z$. A helix is thus generated which contains $p$ monomeric units and $P$ pitches within the period $c$ (helix type succession).

2) Repetition of isoclined alternately enantiomorphous equivalent units: through the operation of a translation $c/2$, accompanied by a reflection in a plane containing the axis of the chain (glide-plane type succession).

3) Repetition of isomorphous alternately anticlined equivalent units: along a helix associated with twofold axes perpendicular to $z$.

4) Repetition of enantiomorphous anticlined equivalent units: through a translation along $z$ associated with a symmetry plane perpendicular to $z$ or a symmetry centre.

All head-to-tail crystallizable polymers, in which the two possible chain directions are intrinsically non-equivalent $\Big($for instance, a polyamide $(-(CH_2)_m-NH-CO-)_n$ or 1-4 polyisoprene  $(-CH_2-CH=CH-\overset{\displaystyle CH_3}{\overset{|}{C}H}-)_n\Big)$ must be built up in the crystal of *isoclined* equivalent units. Hence, only the helix and the glide-plane type structures are possible. In particular, a polyamide containing asymmetric carbon atoms, such as a crystalline protein, must necessarily have a helix type chain structure.

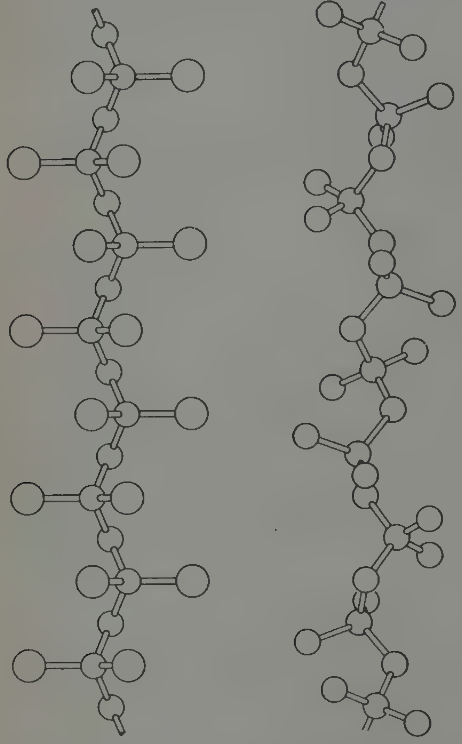

a) b)

Fig. 4. - Model of the assumed structure of (left) polyvinylidene chloride (glide-plane type) as compared with the one found by A. LIQUORI [42] for (right) polyisobutylene (helix type).

All the four types of regular repetitions, described by us, are possible for vinyl head-to-tail polymers. In fact, for these polymers, the two possible chain directions can be considered intrinsically equivalent; however, we must distinguish two intrinsically different (that is stereoisomeric) types of regular successions. Isotactic polymers are the vinyl polymers able «per se» to assume a helix type structure (or, eventually, the structure type 4). Syndiotactic polymers are the vinyl polymers able «per se» to assume a glide-plane type structure (or, eventually, the structure type 3).

Other polymers, as we shall see later, may be expected, from the point of view of the equivalence postulate only, to crystallize in both the helix or the glide-plane type structure, without any intrinsic difference of stereoisomeric type (Fig. 4) (polyisobutylene, helix type; polyvinylidene chloride, probably glide-plane type). This happens when the *monomeric unit* (for instance $-CH_2-CR_2-$) by not prohibited rotations around single bonds, may assume a conformation superposable with its mirror image.

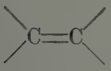
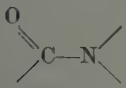
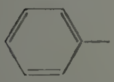
The general rules, above outlined, require, for their practical application to the study of new structures, a knowledge of the conformation that the chain is likely to assume in the crystalline state. We should expect that the conformation of the portion of chain, which takes part in a crystalline zone, is the one which nearly corresponds to a minimum of potential energy for the molecule in free conditions (*e.g.* in the melting or in ideal solution) under the restrictions imposed by the equivalence postulate.

The actual conformation of the chain has in turn a great influence in determining the possible modes of packing of the chains in the crystal, and some physical properties of the polymer, such as the temperature and entropy of fusion.

2·2. *Shape of the macromolecule in the crystal state.* – Stable conformations of a chain should in principle satisfy, as it happens for low molecular weight compounds, the following conditions:

1) Bond length conditions [7].
2) Bond angle conditions [8].
3) Planarity of certain groups of atoms [9].
4) Staggered carbon-carbon bonds.
5) As comfortable as possible Van der Waals distances between non-bonded atoms within the chain.

TABLE I. – *Significant atomic distances and bond angles observed in polymers examined in this and in other papers of this series.*

| | |
|---|---|
| C—C . . . . . . . . . . . . . | 1.54 Å |
| C=C . . . . . . . . . . . . . | 1.32 Å |
| C—C (benzene ring) . . . . . . | 1.40 Å |
| C—C—C . . . . . . . . . . . | 110° ÷ 116° |
| C=C—C . . . . . . . . . . . | 120° ÷ 125° |
| C—C—C (benzene ring) . . . . | 120° |
|  . . . . . . . . . . . | all bonds in a plane |
|  . . . . . . . . . . | all bonds in a plane |
|  . . . . . . . . . . | all bonds in a plane |

A compromise between these 5 conditions is generally achieved in actual structures, as we shall see later in more detail.

There is no need to illustrate the first three points: a discussion is only needed for the two last ones.

1) Principle of staggered bonds. The fourth point was emphasized first by Pitzer and coll. [10] with regard to low molecular weight hydrocarbons, such as butane. He showed, on the basis of thermodynamical calculations, that the trans conformation of the butane chain was more stable than the gauche conformation, both conformations however lying in a minimum of potential energy. Cis conformations of the butane chain are, on the contrary, thermodynamically unstable. C. W. Bunn was the first who applied [11] these ideas to the conformation of polymeric chains, and we could confirm them in a great number of cases. Because of its importance, the fourth point needs a detailed discussion.

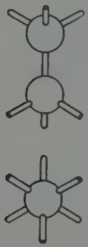


Fig. 5. – Positions of minimum energy of the valence bonds of two tetrahedral singly linked carbon atoms (side and end views).

If one considers two carbon atoms $C_1$ and $C_2$, joined by a single bond, the positions of minimum energy of the other bonds coming out from $C_1$ and $C_2$ are those outlined in Fig. 5. This is probably due to repulsions between localized bonding electron pairs [12]. The application of this principle alone is not sufficient to find out which conformation will be assumed by a linear saturated chain. The number of possible stable conformations is however limited by the equivalence postulate and by condition 5 of this paragraph, which implies that carbon-carbon bonds tend to be more far off than C—H bonds, favouring the trans conformation. Thus we arrive, for an unbranched crystallizable paraffin, at a planar zig-zag structure of the whole chain. The presence of lateral methyl or more bulky groups, may lead to a gauche conformation of the chain, which is the reason of the threefold helical form assumed by the molecules of isotactic polymers. Evidently comfortable accomodation of bulky lateral groups is not compatible with the maintenance of a planar zig-zag chain for isotactic polymers. As examples, in Fig. 6 the structures of chain elements of polyethylene and polypropylene are shown. In Fig. 7 a model of the chain of poly-alpha-butylene is compared with a model of the staggered structure of diamond.

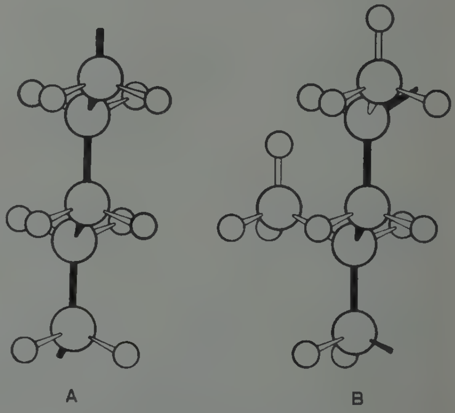


Fig. 6. – Elements of polymer chains: Polyethylene (*A*), Polypropylene (*B*).

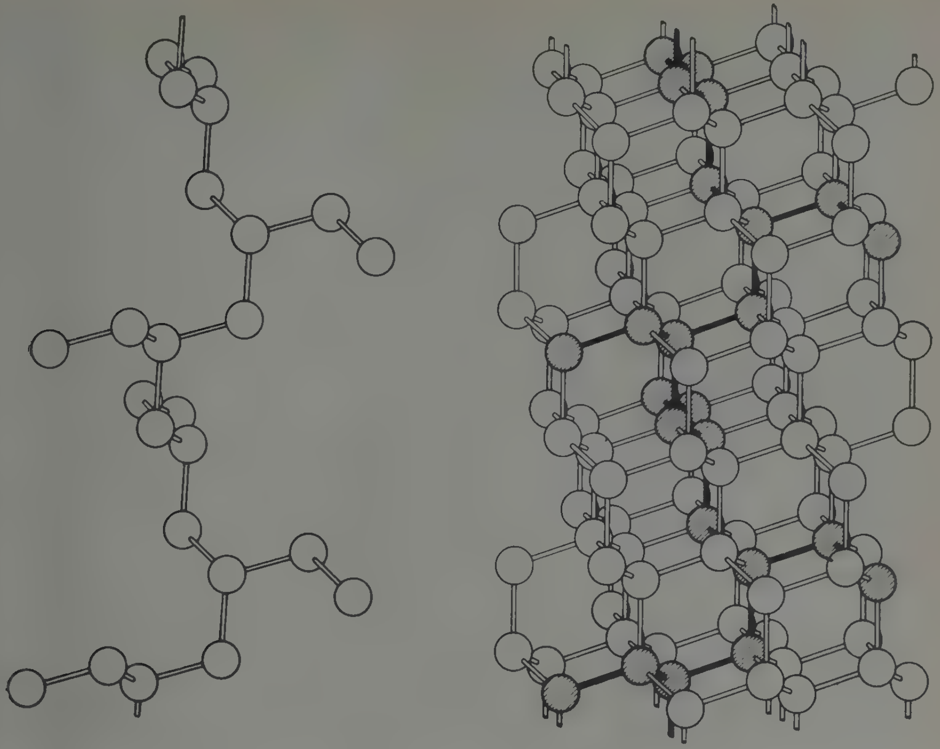


Fig. 7. – Model of the poly-alpha-butylene macromolecule: carbon atoms are staggered as in the diamond lattice.

If a double bond comes out from a carbon atom, it must be considered, with regard to the orientating effect on the other single bonds, as lying in a plane normal to that containing the two remaining single bonds. The $\pi$-electron concentration in this perpendicular plane probably influences the direction to be assumed by the remaining bonds of successive carbon atoms. It has been indeed emphasized that the most probable distribution of electrons in a double bond is the one in which two electron pairs lie in opposite sides of the plane defined by the other four bonds [13].

The resulting effect is that the single bonds adjacent to the double bond are in staggered positions, while the double bond is not (Fig. 8). As a consequence of that, a portion of chain containing four carbon atoms and a central double bond is planar, but the successive carbon atoms tend to be no more in the same plane (Fig. 9).

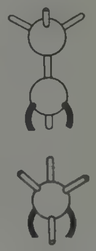


Fig. 8. – Positions of minimum energy of the single bonds of a carbon atom singly linked to a double-bonded one (side and end views).

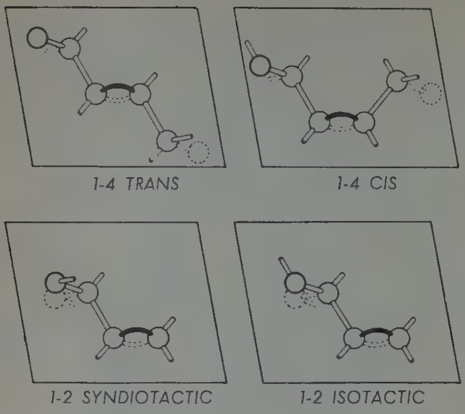


Fig. 9. – Conformation of carbon-carbon bonds adjacent to double bonds, as found in crystalline polybutadiene isomers.

This tendency explains, as we shall see later, in particular cases, the conformation assumed by the monomeric units in all four crystalline polybutadiene stereoisomers (Fig. 10).

2) Van der Waals contacts. As we have already seen, Van der Waals repulsions, we dealt with in the fifth point set up in this section, are extremely important in determining the form of the chains, when atoms, large in comparison with hydrogen, or lateral chains are bonded to an aliphatic chain.

Indeed, an approach of two atoms

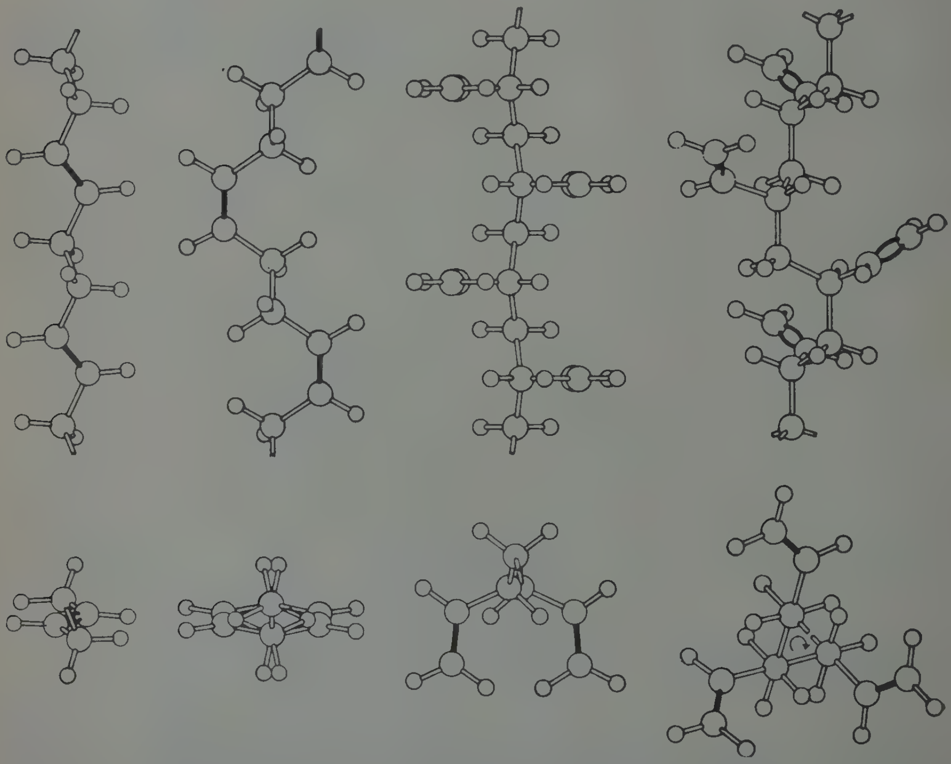


Fig. 10. – Chain conformations of the four crystalline polybutadiene stereoisomers as determined in our Institute.

not directly bonded at a distance below the one consented by Van der Waals forces leads to a large increase of potential energy, which opposes this approach.

Qualitatively correct Van der Waals distances between two atoms may be calculated on the basis of the additivity of Van der Waals covalent radii, when electrostatic interactions of the type involved in hydrogen bridges take no role [14]. Approximately, Van der Waals radii are 0.8 Å greater than the corresponding covalent radii. They cannot however be precisely defined, because only in a rough approximation atoms may be considered spherically shaped and therefore they much depend on the relative positions of the atoms and on the shape of the electron clouds.

The determination of the most probable shape of the macromolecule involves reconciliation of the five rules outlined above with the equivalence postulate to approach a minimum of potential energy. In many instances indeed, these five rules cannot rigorously hold together, expecially when substituents of large dimensions are present along the chain. For instance the lower heat of polymerization of isobutylene, as compared to the one of ethylene, should be attributed, partially at least, to the greater energy content of the chain $C_nH_{2n}$ of polyisobutylene, in comparison with polyethylene, caused by the deformation of the bond sequence due to steric hindrance (as two $CH_3$ groups are joined to every two carbon atoms along the chain).

As a consequence of the minimum energy postulate, we may expect in some instances, while rules 1 and 3 are always holding:

1) A deformation of bond angles exceeding the normal values (*e.g.* more than 110° for C—C—C angle).

2) A modification of the form of the main chain contrasting the principle of staggered bonds.

3) A greater approach of certain atoms in the chain, at distances a little below normal Van der Waals ones.

In general the above-mentioned deformations of the various types of chains, take place simultaneously, but in different degrees, in order to approach a minimum of potential energy. For the prediction of the most stable conformations, the engineering principles used in the study of elastic structure deformations should be appliable [15].

Consequences of such deformations, to be discussed more deeply later, are, for instance, the non-planarity of the zig-zag chain of syndiotactic 1,2 polybutadiene, the deformation of bond angles in polypropylene, the four-fold instead of three-fold helix structure of poly-3-methylbutene.

The above outlined principles, which regard only interactions between atoms in the same chain, are of general character and should be sufficient to establish the preferred conformations of small portions of chains also in the free state.

Also, in most cases and especially for hydrocarbon polymers, they allow us to predict, together with the equivalence postulate, the conformation to be assumed by a single chain in the crystalline state. As we have already noted, however, the need of uniformly filling space may cause slight modifications in the form of the chain from the one foreseeable as that of minimum energy in the free state.

2·3. *Mode of packing of the chains.* – The order in three dimensions of polymer chains to give a crystal may be only realized by a parallel orderly association of the chains, with contacts between atoms of different chains not exceeding the Van der Waals contacts established for low molecular weight compounds (see Table II).

TABLE II. – *Van der Waals contacts observed in polymers examined in this and in other papers of this series.*

| | |
|---|---|
| $CH_3$ – —$CH_3$ | $4.0 \div 4.3$ Å |
| $C_{ar}$ — —$C_{ar}$ (benzene ring) | $3.5 \div 3.8$ Å |
| $CH_2$— —$CH_3$ | $4.0 \div 4.3$ Å |
| H — —H | $2.4 \div 2.7$ Å |

When, as it frequently occurs, both up and down molecules are represented in the unit cell, the space-group is such as to allow the presence in the lattice of anticlined chains in equivalent positions. When from a given monomeric unit equivalent right and left-handed helices are likely to be built up (for example from a monomer not containing asymmetric carbon atoms, like propylene) both are often represented in the crystal lattice, and the space-group is such as to allow the presence of enantiomorphous chains in equivalent positions; it may occur however that when bulky side groups are present along the chain, a suitably dense packing can be obtained only in space groups in which uniquely isoclined or uniquely isomorphous helices are accomodated.

For instance, whereas in the structure of polybutylene both up and down molecules may be accomodated, only isoclined molecules are present in the closely related structure of poly-o-fluoro-styrene [16]. There is increasing evidence that in some cases *i.e.* in the case of isotactic poly-t-butylacrylate only isomorphous helices can be accomodated in the same crystal [17] so that a separation of optical antipodes occurs on crystallization from the melt, when it contains both right and left-handed helices. In other cases, isomorphous helices provide a good filling of space only through a superspiralization, as in some proteins [18].

It frequently occurs that nearly isosteric (*e.g.* with a similar steric encumberment) equivalent chains (*e.g.* enantiomorphous isoclined, or isomorphous anticlined, or enantiomorphous anticlined) may vicariate themselves in the same lattice site. This phenomenon has been observed for the first time by NYBURG in natural rubber, in the crystal lattice of which, a statistical substitution mirrored chains is possible [19].

We have observed it in isotactic polymers [20], and found evidence for its existence also in guttapercha and polychloroprene [21].

Generally, in the packing, the polymer molecules tend to maintain, partially at least, the symmetry of the chain. For instance, in the structure of polymers whose chains are of the glide-plane type, the glide-plane is usually maintained in the lattice. This fact occurs in natural rubber, as well as in polyvinylchloride, syndiotactic 1,2 and cis 1,4 polybutadiene and rubber hydrochloride [22]. The threefold helical symmetry of the chain of poly-α-butene, polystyrene and poly-o-fluoro-styrene, so as the fourfold helical symmetry of the chain of polyvinylnaphtalene and poly-o-methylstyrene, are maintained in the respective crystal lattices [23].

In the parallel association of chains to provide polymer crystals, we often recognize ordered layers of macromolecules on planes by the parallel or antiparallel association of which we may imagine that the crystal is formed. These planes are defined by the chain axis and by one of the smallest crystallographic translations equatorial to the fiber axis. The value of both translations defining these planes are scarcely affected by thermal movements, so that thermal expansion occurs almost completely in a direction perpendicular to these planes [24].

We shall call them, whenever recognizable, «principal planes». They contain in general, as it was mentioned above, two crystallographic axes: the fiber axis and what we shall call « principal equatorial axis ». It is very likely that along this axis the polymer crystals may grow at their best, because generally we find it in the direction of growing of the spherulites, as we may conclude from the known structure of spherulites of polythene, polypropylene, and nylon [25].

With these background principles we shall now discuss in a more detailed way the structure of some crystalline polymers which have been studied by us.

## 3. – The structure of some crystalline polyhydrocarbons.

3·1. *Polymethylene.* – Polymethylene, that is the polymer obtained by catalytic decomposition of diazomethane, is the simplest completely linear hydrocarbon polymer. Its structure is the same as that proposed by BUNN for the crystalline part of I.C.I. polyethylene [26]. The zig-zag structure of the chain

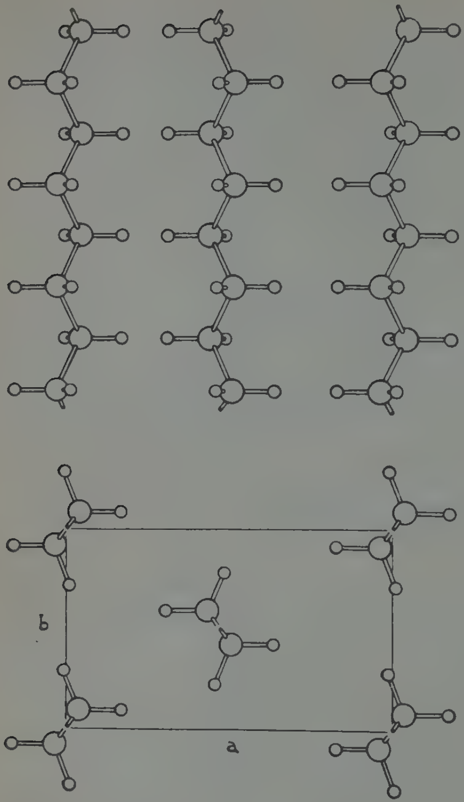


Fig. 11. - Model of the crystal structure of polymethylene.

has already been discussed in this paper, in connection with the equivalence postulate and minimum energy considerations: equivalent isomorphous —$CH_2$— groups repeat themselves along a two-fold helix. The nearly cylindrical molecules fit themselves in a quasi hexagonal array (Fig. 11).

3·2 *Isotactic polymers.* – Isotactic polymers are the cis stereoisomers of the vinyl head -to-tail polymers, as we have already quoted in Section **1**. The bulky dimensions of lateral groups do not allow for these polymers a planar chain conformation. A planar structure is indeed impossible, because the distance of 2.5 Å (if we consider for example polypropylene), that should come out between the nuclei of two carbon atoms of successive methyl groups is such, that certain hydrogen atoms of the methyl groups would result too near to each other, in contrast with minimum energy requirements [26]. The nature of the strain may be easily understood when we consider that the large resonance energy of polyacetylene, which has a planar structure and is crystalline, is destroyed in polypropine, whose chain structure is non-planar, with a net loss, according to our calculations, of about 10 kcal per monomeric unit (something like happens with benzene and cyclooctatetraene) [27, 28].

A suitable accomodation of the methyl groups may be achieved in a helix type structure, imposed by the equivalence postulate, and in accordance with the principle of staggered bonds, only when the successive monomeric units are arranged on a three-fold helix.

This structure may be easily carried out from the planar one, sketched in Fig. 12-*a*), by effecting rotations of 120° around bonds $L_1$, $L_2$, $L_3$ or around bonds $L_{1'}$, $L_{2'}$, $L_{3'}$ respectively clock-wise or anticlock-wise; thus generating a left- *c*) or a right-handed *b*) helix. The methyl separation achieved in this way is comfortable ($> 4$ Å) and the staggered bonds principle is respected. As the planar configuration is strongly unfavoured from a thermodynamic point of view, no interconversion of enantiomorphous helices appears to be likely at low temperatures, and we may consider left and right-handed helices as optical stereoisomers.

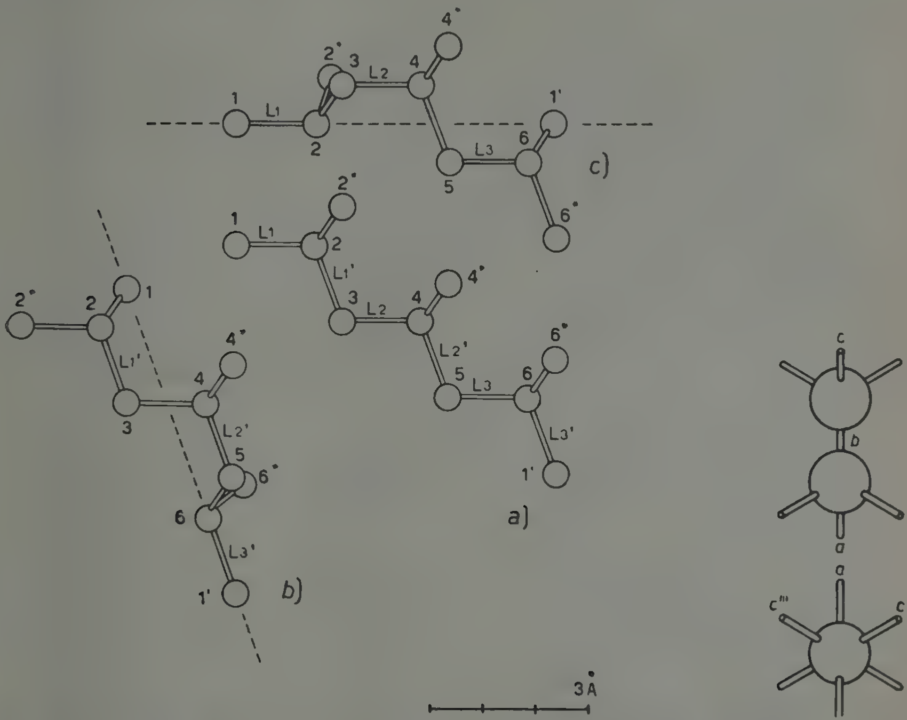


Fig. 12. – Actual conformation of isotactic polypropylene chain as derived from the planar chain structure.

Optical activity is prevented from the presence of an equal quantity of the two forms.

When built up with normal bond lengths (1.54 Å) and angles (109° 30′) the isotactic threefold helix should have an identity period of 6.2 Å; actually for polypropylene an identity period as large as 6.5 Å has been observed. A slight enlargement of C—C—C angles along the chain appears to be the reason of this fact, owing to a more confortable accomodation of Van der Waals contacts between the hydrogen atoms of the chain. The bulkiness of side groups, and more precisely, the steric encumberment of side groups in proximity of the chain is, on the contrary, the reason why 3-methyl substituted polyolefins have a four-fold helix structure in the crystalline state, and 4-methyl substituted ones a 3.5-fold helix structure. The staggered bonds principle is no more rigidly respected, but valence angles along the chain tend to approach the normal ones again, so that very low differences in energy should be present between a three-fold and a four-fold helix [29] (Fig. 13).

Thus, poly-α-butene, for instance, has been observed to be crystallizable in both forms, the four-fold one however being the least stable [30]. It has been concluded, from the fact that this form is the first which appears on crystallization both from the melt or from a solution, that in the liquid state there is a certain degree of freedom with small energy intakes, to rotation around single bonds in the chain, in the sense of a slight despiralization of the chain.

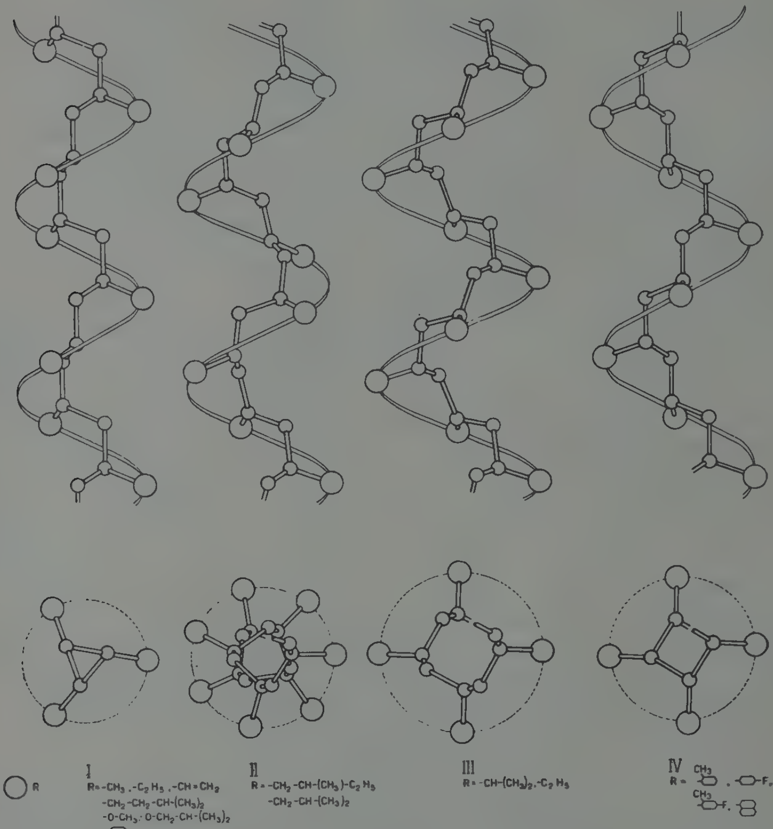


Fig. 13. – Models of helicoidal chains found for different isotactic polymers.

It is interesting to note that the four-fold helix poly-α-butene crystals are suddenly transformed in the three-fold helix ones by drawing, or by pressing and, more slowly, on standing at room temperature.

Other different forms of chains, slightly modified from the above mentioned ones, may also appear in crystalline isotactic polymers. For example, poly-o-methylstyrene has a four-fold helical chain structure different from the one described for aliphatic polyolefins (Fig. 13), whereas poly-m-methylstyrene has a 3.67-fold helical chain structure (11 monomeric units in three pitches

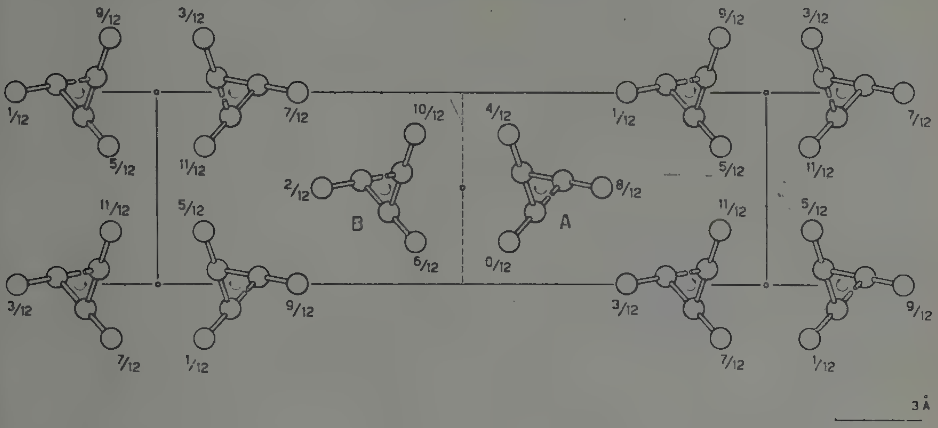


Fig. 14. – Mode of packing of polypropylene chains in the crystal.

along the identity period). Much complicated chain structures, which have not yet been completely examined, have been observed for other substituted polystyrenes. The reason of such a variety of different forms is to be found

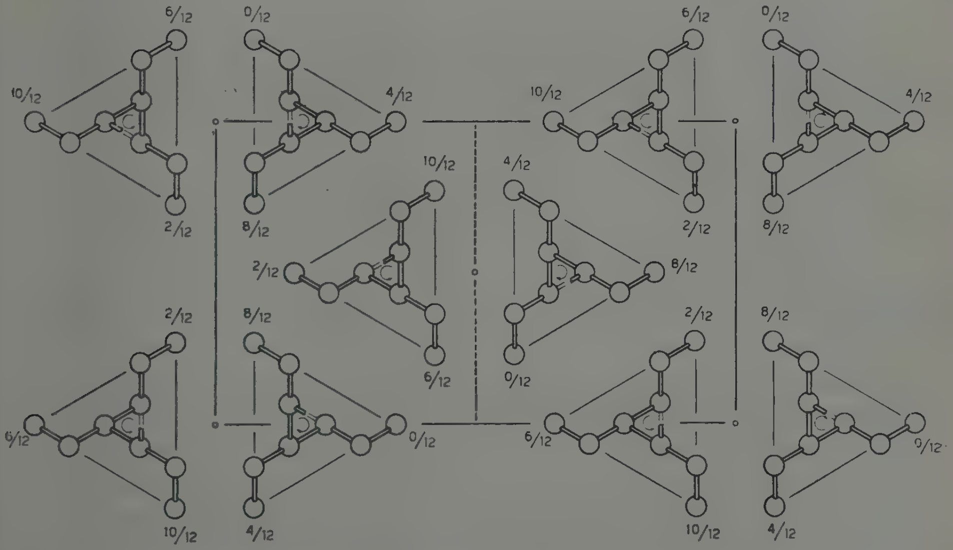


Fig. 15. – Mode of packing of poly-alpha-butene chains in the crystal.

in the packing requirements, both within the very chain and also among different chains, the side groups of substituted polystyrenes being very stiff and bulky indeed. The solution of the complete crystal structure of polypropylene and poly-α-butene effected by us [31] permits a discussion of the mode of packing of the chains of these isotactic polymers in crystals (Figs. 14, 15).

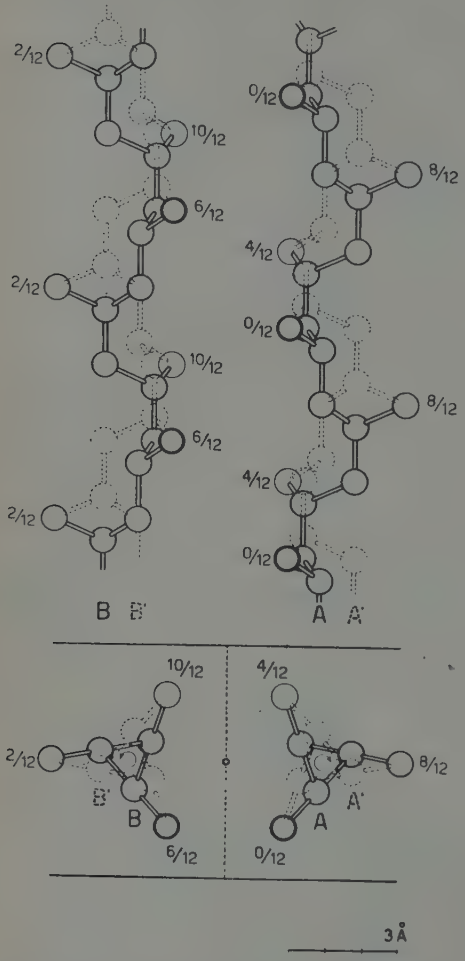


Fig. 16. – Model showing isosterism of anticlined isomorphous chains of polypropylene in a crystal.

On considering the packing requirements explained in Sect. 1, the lattice of an isotactic polymer should possibly accomodate in equal quantity enantiomorphous chains, presumably through operations of symmetry of the space group.

According to the requirements just explained, it is actually found that, in all these polymers, enantiomorphous chains face each other in pairs, a close packing being realized through the operation of a glide-plane with translation parallel to the fiber axis. Moreover, anticlined isomorphous chains of the isotactic polymers of propylene and α-butene are nearly isosteric, when we refer to the encumberment of lateral groups (Fig. 16) and as long as intermolecular contacts are realized almost uniquely by these lateral groups, anticlined isomorphous chains may in principle vicariate in the same lattice site. In fact it is thought that each crystal of these polymers is composed of very small blocks of anticlined crystallites built up of isoclined chains, so that diffraction phenomena may be easier interpreted supposing that anticlined isomorphous chains may statistically vicariate in each site of the crystal.

Poly-α-butene (and the closely related isotactic poly-1,2-butadiene) are able to maintain the complete symmetry of the chain, so that three glide planes making angles of 120° among themselves and related by a three-fold screw axis are easily recognizable in the rhombohedral structure of these polymers.

A too loose mode of packing should result when a similar structure is supposed to be likely also for polypropylene.

The glide plane, through which two enantiomorphous facing chains are related, turns out to be, in this case, a principal plane. Evidence that the *a-c*

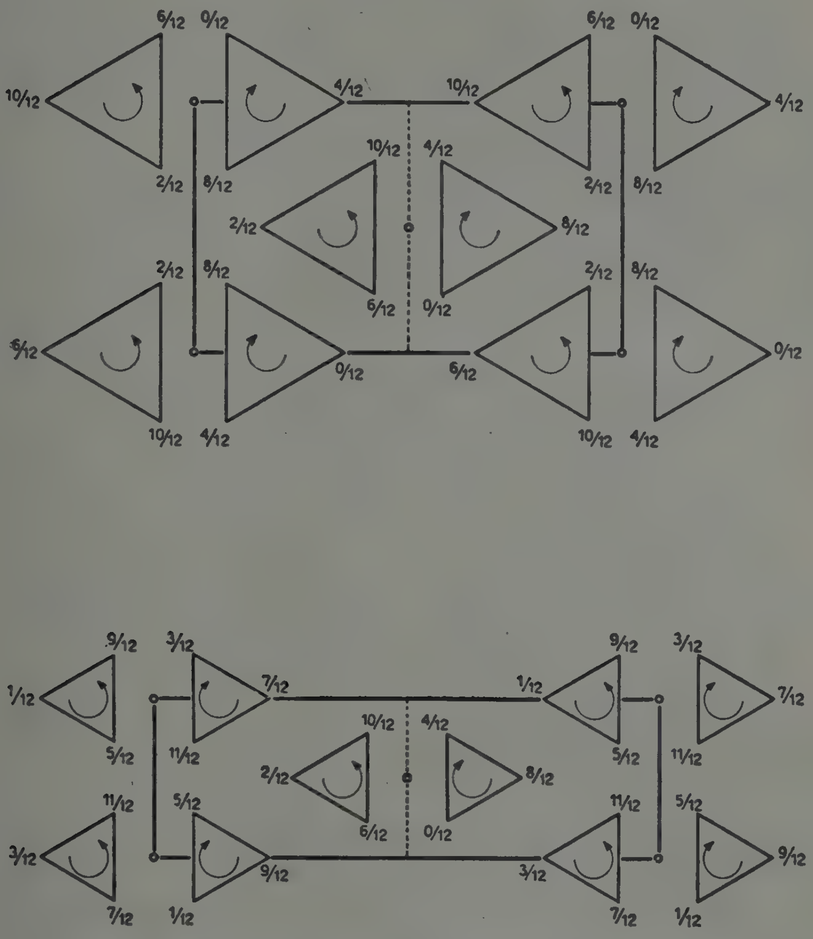


Fig. 17. – Comparison between the mode of packing of polypropylene and poly-alpha-butene in the crystal state.

plane is a principal plane in polypropylene is found in the close-packing realized along this plane of the side groups of two enantiomorphous symmetry related chains (Fig. 17) and hence in the shortness of the *a*-axis, in its parallel orientation along the radii of spherulites and in its very low thermal expansion, as compared to the one taking place along the *b*-axis.

The mode of packing of four-fold helix polyvinylnaphtalene and poly-o-methylstyrene is also obtained through the operation of glide-planes between enantiomorphous chains, as it is possible to see in the Fig. 18.

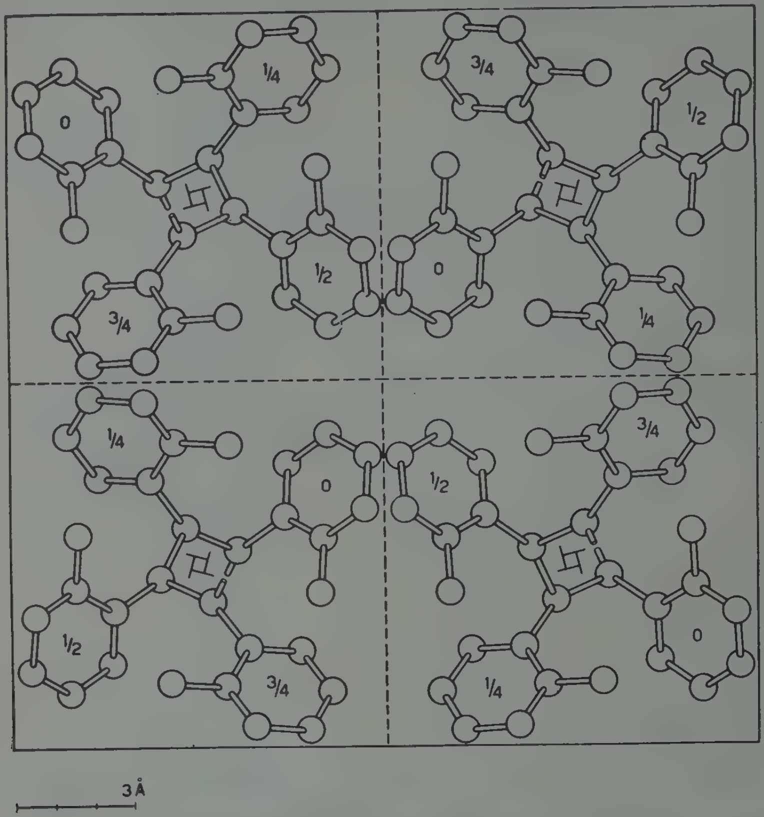


Fig. 18. – Model of packing of poly-ortho-methylstyrene chains in the crystal.

3·3. *Syndiotactic polymers.* – Syndiotactic polymers may be defined as trans stereoisomers of the vinyl head-to-tail polymers.

Their chain structure may be, according to the equivalence postulate, of the glide-plane type, hence repetition being achieved along the fiber axis every two (σὺν δύο) monomeric units, or their chain may follow a helix associated with perpendicular twofold axes (*).

Now it is known that two polymers possess a syndiotactic chain structure: polyvinylchloride and one of the two crystalline stereoisomers of 1-2 polybutadiene [32].

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(*) *Note added in proof.* – This is the type of chain recently found by the AA. for syndiotactic polypropylene. The model is shown in Fig. 1 of the introductory paper of this series.

The bulkiness of the side groups of these two polymers does not hinder, as was the case of isotactic polymers, a planar or nearly planar conformation of the chain. Only with regard to polybutadiene a slight deviation from a completely zig-zag planar structure of the chain has been supposed, but not thoroughly confirmed, owing to steric repulsions between successive lateral vinyl groups, the perpendicular orientation of which in regard to the chain axis obeys the principle of staggered bonds (Fig. 19, see also Fig. 9). In every case it is easy to see on inspection that no distinction is needed between up and down molecules, and in the lattice we have to accomodate only one type of chain.

The glide plane is maintained in the unit cell of these polymers. The molecules pack closely in layers along this plane. The crystal is built up of many antiparallel layers packing at their best between themselves.

The thermal expansion occurs almost completely in syndiotactic 1,2 polybutadiene in a direction perpendicular to the glide-plane, according to the phenomena connected with the supposed existence of a principal plane of packing.

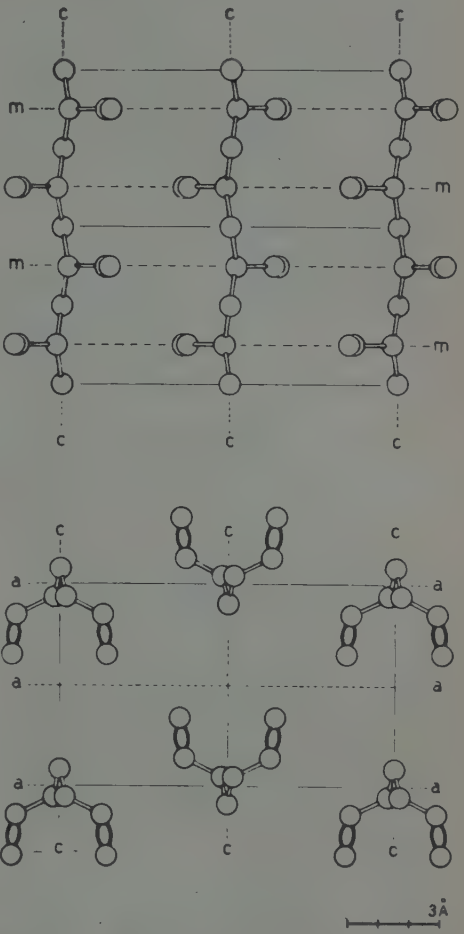

Fig. 19. Model of packing of syndiotactic, 1-2 polybutadiene in the crystal.

3·4. *Crystalline* 1,4 *polydienes.* – Under the heading of isotactic and syndiotactic polymers we have dealt with the known structure of 1,2 stereoisomeric polydienes. In this chapter we shall deal with the known structures of crystalline 1-4 polydienes. The synthesis of all four crystalline stereoisomers of polybutadiene and the study of their structure effected in the Institute of Industrial Chemistry of the Polytechnic of Milan, permits now to have a clearer idea of stereoisomeric phenomena in the field of polydienes.

*a*) *Cis* 1,4 *polydienes.* – Natural rubber is the regular head-to-tail polymer built up of cis 1,4 isoprene units. Its chain structure may be expected uniquely in one of two types of successions, the glide-plane and the helix-type succession. However it is impossible, on the basis of the equivalence postulate only, to establish which of the two forms will be actually chosen by the macromolecules on crystallization, as they would not correspond to intrinsical differences in the configuration of the chain.

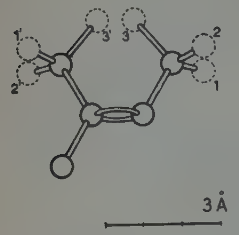

Fig. 20. – Possible conformations of 1-4 cis isoprene unit satisfying the principle of staggered bonds.

Actually a glide-plane non-planar structure is found for the chain of crystalline cis 1,4 polyisoprene [33]. Indeed on the basis of minimum energy considerations we should expect that:

1) the five atoms of each monomeric unit be in a plane;

2) the direction of the $CH_2$—$CH_2$ bond, should take, in accordance with the principle of the staggered bonds, any of the three positions outlined in Fig. 20. Positions 3 and 3′ must be discarded because of excessively short Van der Waals contacts between atoms of the same chain;

3) the directions of the two $CH_2$—$CH_2$ bonds on the two sides of the isoprene unit should be in opposite and parallel directions; *i.e.* the enantiomorphous conformations 1-1′ and 2-2′ are best likely to be realized;

4) repetition of a monomeric unit with such a conformation, may be achieved in a helix type or in a glide-plane type succession, the first possibility being discarded because of unsuitable contacts between the methyl group and some chain carbon atoms.

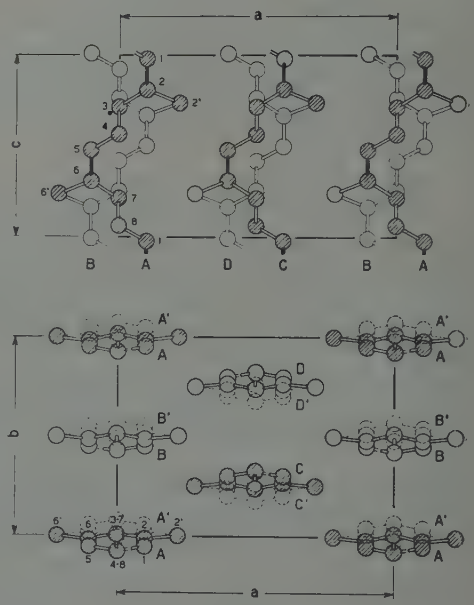

Fig. 21. – Model of the structure of 1-4 cis polyisoprene.

The glide-plane is maintained in the lattice, according to a common feature occurring in many studied polymers, so that a close packing of molecules is expected along this plane; also, alternatively up and down molecules should be represented along this plane.

As the contacts lateral to the principal plane thus realized are due only to methyl groups, we find that, in the actual structure, successive parallel or antiparallel principal planes (*bc*) are able to pack themselves at random. It is possible to see from Fig. 21 that a layer of molecules such as A—B—A—B can be followed equally well by a layer such as C—D—C—D or C′—D′—C′—D′—.

Perhaps, we may explain the low melting entropy of rubber in comparison with the one of guttapercha, by supposing that, in the molten state, not only a certain degree of parallelism between the chains is maintained, but also that the flexible ribbon-shaped molecules tend to maintain some kind of parallel association of the ribbons.

A great similarity of structure is to be expected between [34] cis 1,4 polybutadiene and cis 1,4 polyisoprene: actually a similar conformation of the chain was found by us, in which enantiomorphous monomeric units repeat along a glide plane. No more distinction however, is needed in cis 1,4 polybutadiene as compared with cis 1,4 polyisoprene between up and down molecules; also, one finds an identity period slightly longer than the one foreseeable on the basis of the staggered bonds principle; this fact is probably due to repulsions between hydrogen atoms of two $CH_2$ groups, in opposite position relative to the double bond, which tend to lengthen the chain; repulsions which could not be eliminated in the case of polyisoprene because of the steric hindrance provided by the methyl group (Fig. 22).

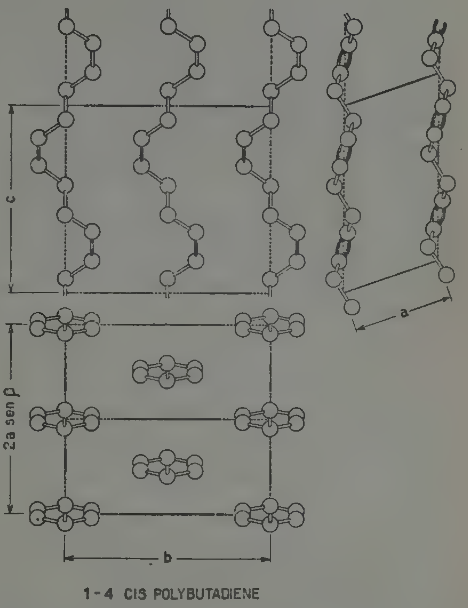

Fig. 22. – Model of the structure of 1-4 cis polybutadiene.

The glide-plane may be also considered a principal plane in polybutadiene, and determines a mode of packing of the macromolecules in the crystalline state, which is very similar to, but simpler than, that realized in the structure of polyisoprene. In fact, there is no more need for accomodation of up and down molecules, nor for statistical distribution of successive antiparallel or parallel layers of molecules developed on the principal plane, owing to the absence of lateral groups.

*b*) *Trans* 1,4 *polydienes*. – The structure of guttapercha, the trans 1,4 head-to-tail stereoisomer of polyisoprene, was thoroughly studied for the first time by C. W. BUNN [35], who assessed the principal features of the structure of one of the three crystalline forms in which this polymer may occur ($\beta$ form).

Some strangeness of the chain structure was eliminated by JEFFREY [36], supposing and proving that the five atoms of each isoprene unit must be in a plane.

As a matter of fact, successive trans isoprene units may repeat according to the principle of the staggered bonds in various ways without any great difference in regard to sterical hindrances and, according to this fact, different identity periods have been found for the three different crystalline forms in which guttapercha may occur; and yet, however, there is no complete agreement as to the form of the chains, reported from different authors.

In accordance with the equivalence and minimum energy postulate, we tentatively proposed, the three forms shown in Fig. 23, whose calculated identity periods are in accordance with literature data [37].

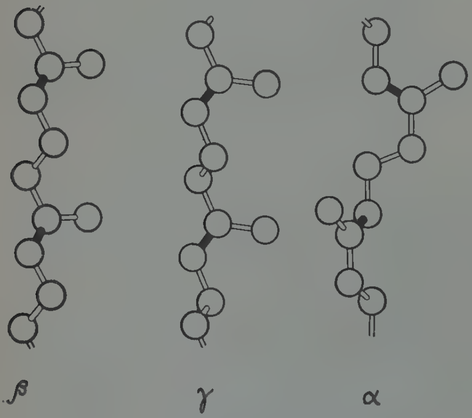

Fig. 23. – Models of the chain of guttapercha (trans 1-4 polyisoprene) in different crystalline modifications.

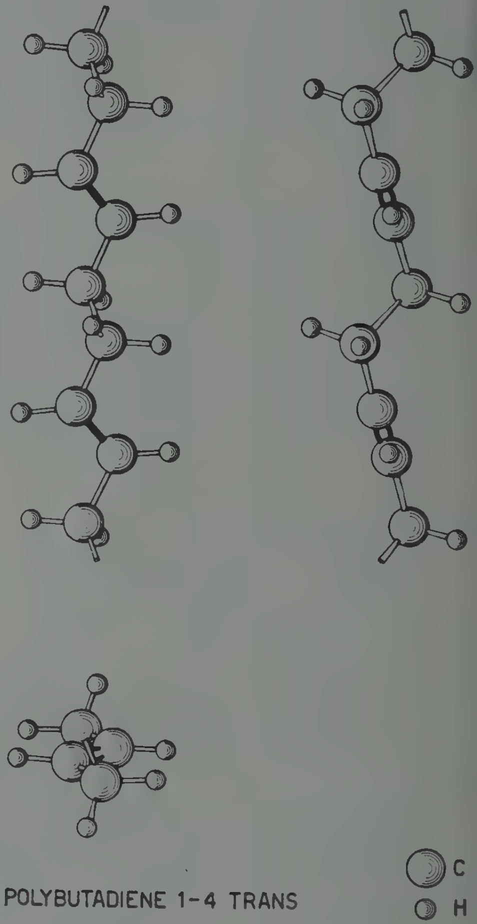

Fig. 24. – Model of the chain of 1-4 trans polybutadiene.

A structure of chain similar to the one of $\beta$-guttapercha is possessed by trans 1,4 polybutadiene, which according to our studies can also appear, in different crystal forms as guttapercha does [38].

This polymer shows in its crystal state at room temperature, a chain structure (with an identity period $c = 4.92$) very similar to that of β-gutta-percha (Fig. 24). The almost cylindrical shape of its molecules favours a mode of chain packing in a pseudo-hexagonal array with $a = 4.54$ Å. At about 65 °C a first order transition in the solid state takes place. The structure of the high temperature phase corresponds to a mode of packing in which the chains, always remaining parallel to each other, should be more free to move and rotate along the chain axes. The phase change is accompanied by a lowering of the density of more than 9%. The low density phase possesses a pseudohexagonal array with $a = 4.88$ Å, $c = 4.68$ Å. In a drawn fiber this transformation gives rise to a sudden reversible contractile process, which is obviously analogous to the one taking place in living muscles.

The dimensional change along the fiber axis corresponds to the change of the $c$ dimension (about 5%). We believe this is the first time that a similar phenomenon has been observed in synthetic fibers, related to a first order crystal-crystal transition.

## 4. – Other notable structures.

The principles discussed in this work with regard to hydrocarbons may be also applied to other notable structures of non-hydrocarbon polymers; so we report some examples to demonstrate the general validity of the principles previously discussed.

*Nylons.* – The form of the chain of nylon is found to be nearly planar in accordance with the principle of staggered bonds [39]. Hydrogen bonds are formed among different molecules in the same plane in which the chain is contained; successively these planes pack themselves at their best. Along these planes the direction of accretion of spherulites is found.

At the melting point [41] we should expect disruption of the lattice prevailingly in a direction normal to this plane. As long as thermal oscillations should occur at their best, owing to lower potential barriers, around $CH_2$—CO— and NH—$CH_2$ bonds, giving rise to typically different deviations from the planar form of the chain, a lower packing efficiency and then a lower melting point should be expected for nylon 6 in comparison with nylon 66 (Fig. 25) and, more generally, for nylons containing odd sequences of $CH_2$ groups in comparison with those containing even sequences of $CH_2$ groups.

There is some evidence that a slight deviation from the completely planar form is present in nylon 66 and nylon 6 even at room temperature. The fact which has not yet been explained that nylons have a lower heat and entropy of fusion than polyolefins or polyethers supports our assumption that hydrogen bonds are statistically maintained on layers also in the melt.

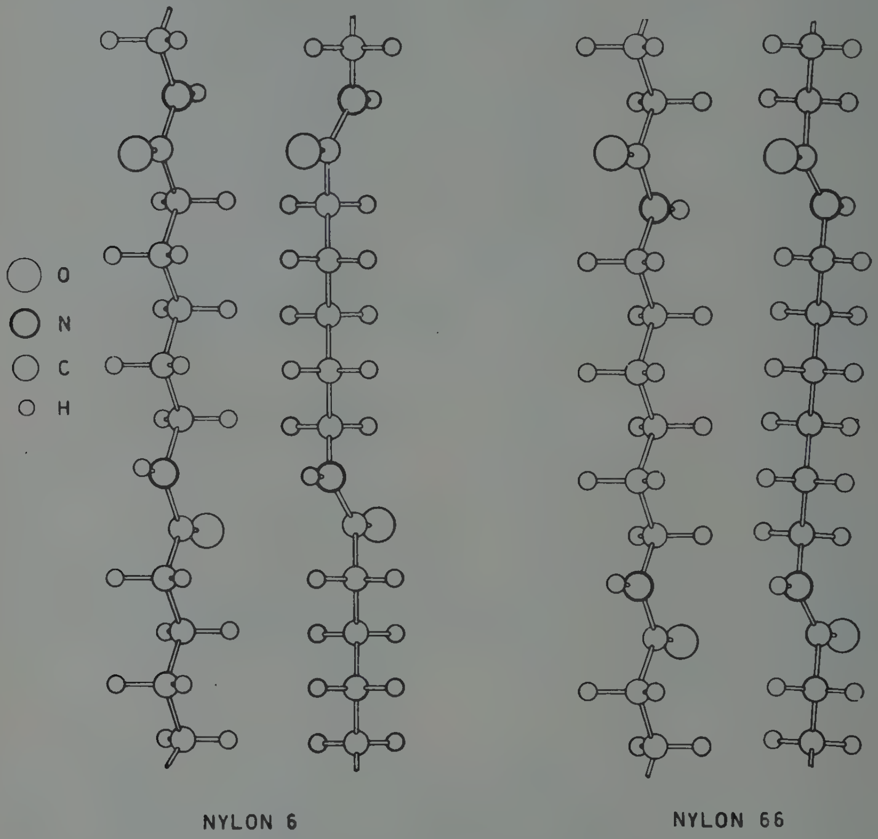

Fig. 25. – Possible models of the chains of nylon 6 and nylon 66 slightly deviating from planarity in a thermal vibration.

*Teflon.* – Teflon is the polymer of tetrafluoroethylene. According to the principle of staggered bonds the best form of the chain should be the planar one; but, owing to repulsions between fluorine atoms, a slight spiralization of the chain occurs, giving rise to a helix along a pitch of which 13 $CF_2$ units repeat themselves [41].

The chains have an almost cylindrical encumberment, so that they pack in a pseudo-hexagonal array.

*Polyisobutene* [42], *polyvinylidene chloride* [43]. – The complete crystal structures of these polymers are not known; but the form of their chains is supposed to be of the glide-plane type for polyvinylidene chloride, and, according to LIQUORI, of the helix-type for polyisobutene as may be deduced from the length of the fiber axis and the principal features of their X-ray spectra. The deviation from staggered structures of their chain is certainly due to the great steric encumberment of the lateral groups (see Fig. 4).

*Poly-propylene-oxide* [44]. – This polymer has been studied by us, and it is of some interest because the monomer contains asymmetric carbon atoms. In fact a helix structure has been found, in accordance with the equivalence postulate, satisfying the minimum energy requirements. When prepared from the racemic monomer, a crystalline polymer is obtained only with stereospecific catalysts, which permit the growing of chains only from isomorphous monomeric units (Fig. 26).

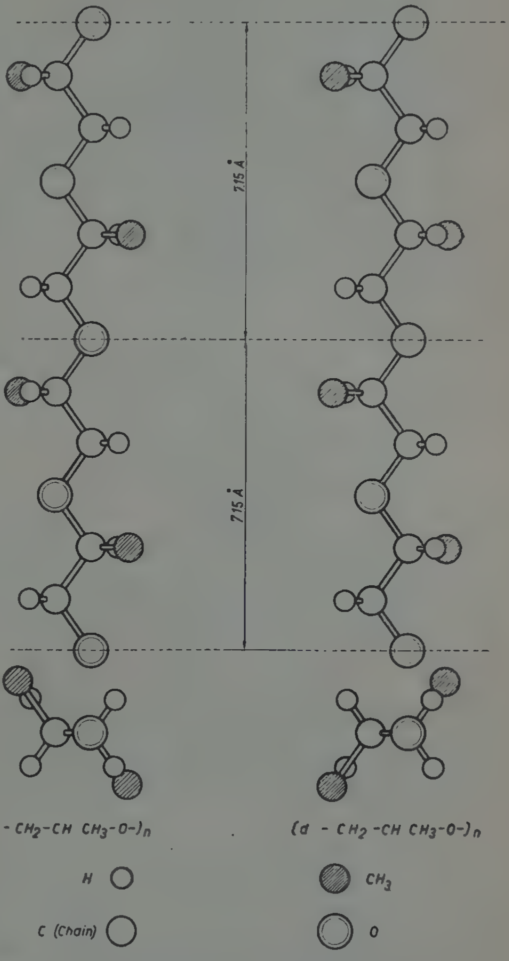

Fig. 26. – Model of the chain of d- and l-polypropyleneoxide.

*Polyvinylalcohol* [45]. – This polymer, notwithstanding the irregular succession of hydroxyl groups, is able to crystallize. Actually, the chain form is similar to that of polyethylene, the OH groups being of a sufficiently small size (in comparison to the H atoms) to be accomodated also in a cis succession. In the crystal structure, the molecules face in pairs, realizing hydrogen bonds between themselves, whenever possible, *i.e.* at random, according to the distribution of the hydroxyl groups.

*Proteins* [46]. – According to whether hydrogen bonds are formed between different chains or in the same chain, two different kinds of helix type structures are possible for the chain: 2-fold helix structures (Fig. 27) (the packing being determined by hydrogen bonds realized on opposite sides of the chain along a principal plane) or more-fold helix structures with the plane of the amide group parallel to the chain axis so as to form intramolecular hydrogen bonds (Fig. 28) within the chain.

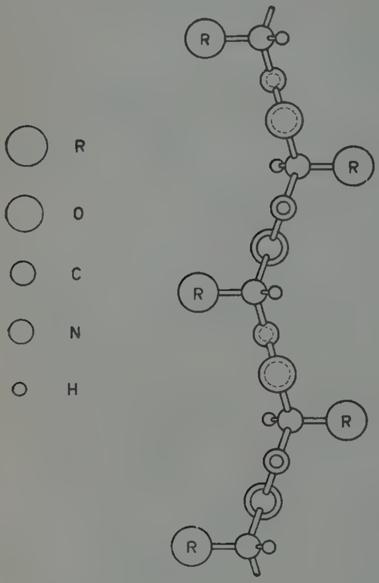

Fig. 27. – Model of the chain of $\beta$ Keratin type proteins.

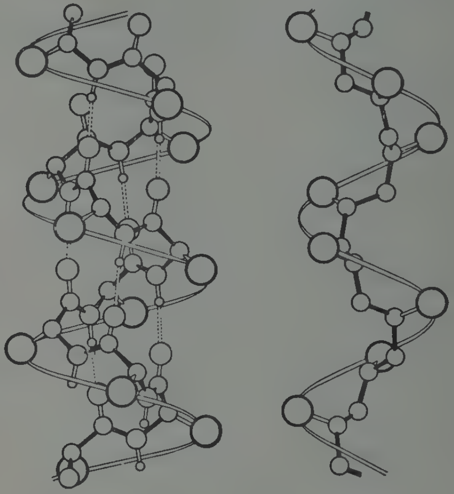

Fig. 28. – Model of the chain of $\alpha$ Keratin type proteins (left), compared with the chain of a 3,5 helix isotactic polymer (right).

*Polysaccharides* [47, 48]. – Cellulose may be considered as the 1,4 connected polymer of $\alpha$-glucose. Successive $\alpha$-glucose residues are able to follow a 2-fold helicoidal path, without strain, satisfying the principle of staggered bonds.

A 2-fold helix path is no more possible for the chain of starch, which is built up of $\beta$-glucose residues, so that a three-fold helix results; close similarity may be found between the chain structures of these two polymers, respectively with the 2-fold helix structure of polyethylene (all « trans » bonds) and with the 3-fold helix structure of polypropylene (alternatively « trans » and « gauche » bonds) (Fig. 29).

The packing of the chains of polysaccharides appears mostly dependent on the formation of strong intermolecular hydrogen bonds.

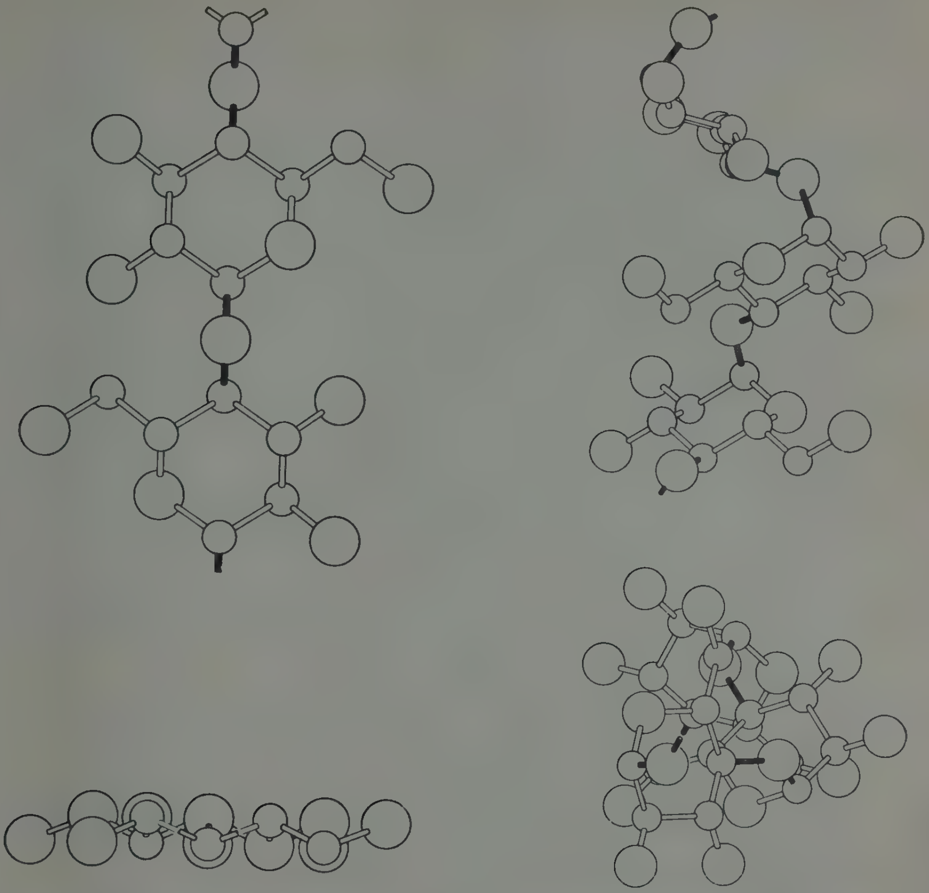

Fig. 29. – Comparison between the chain of cellulose (left) and that of starch (right). The piranic ring is rigid. The black drawn bonds, joining the rigid rings through an ethereal oxygen atom, follow one to another like polymethylene (cellulose) and polypropylene (starch) bonds.

The uniqueness of helix-type structures for the chain of crystalline proteins and polysaccharides follows directly from the equivalence postulate, as the corresponding monomeric units contain asymmetric carbon atoms.

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SUPPLEMENTO AL VOLUME XV, SERIE X
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# Structure and Properties of Isotactic Polypropylene.

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(ricevuto il 26 Giugno 1959)

## 1. – Generalities.

In 1954 we announced the main structural characteristics of the isotactic crystalline polymers of alpha-olefins synthesized first at the laboratory of Industrial Chemistry of the Milan Polytechnic [1].

Many of them, such as polypropylene and poly-alpha-butene, seem to be destined to increase even more their importance as raw materials for the production of plastics and textile fibers in consequence of their excellent thermal and mechanical properties, of their low cost and the versatility of uses.

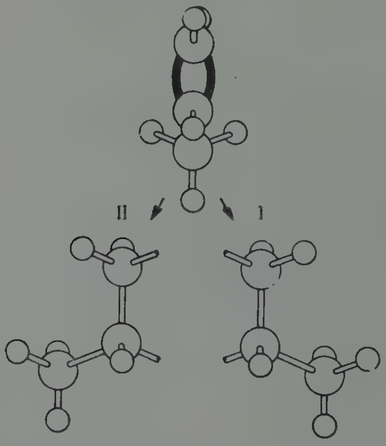

Fig. 1. – Possible configurations that the monomeric unit of propylene may assume.

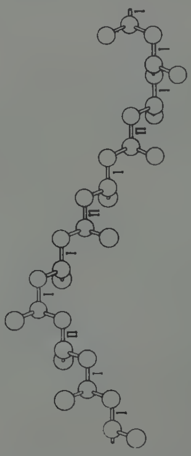

Fig. 2. – Possible conformation of an atactic chain of polypropylene.

In previous works we have demonstrated that the molecules of these crystalline polymers show a high regularity of structure [2], allowed by the peculiar anionic co-ordinated mechanism of the stereospecific polymerization reaction of $\alpha$-olefins. This reaction goes on through successive additions of monomeric units to metal-carbon bonds of complexes formed on the surface of a crystal having a layer lattice, generally the chloride of a transition element (*e.g.* $\alpha$—$TiCl_3$), by the action of a metal-alkyl (*e.g.* $Al(C_2H_5)_3$).

Usually in a head-to-tail but not stereospecific polymerization, for instance in a polymerization with amorphous catalysts and anionic co-ordinated mechanism, the propylene monomeric units may assume two equivalent specular conformations that cannot in any way be superposed (Fig. 1). The resulting polymer is formed by an unordered succession of monomeric units of the two types and the chain has therefore a random steric structure (Fig. 2).

In the above-mentioned reaction conditions of heterogeneous stereospecific catalysis propylene is first assumed to co-ordinate through a $\pi$-bond with the transition element of the catalytic complex, and, therefore, when the polarized olefin molecule is added up to the growing chain, becoming a monomeric unit of the polymer, it can assume only one of the two configurations illustrated in Fig. 1 [3].

Under these conditions the successive monomeric units along the chain assume the same sterical configuration (Fig. 3). We called «isotactic» [4], from the Greek word ἴσος, similar and τάττω, to settle, those vinyl polymers whose monomeric units, which follow one another head-to-tail along the chain, are able to assume by rotation around single carbon-carbon bonds, sterically equal configurations, that is of repeating themselves by simple operations of translation and rotation along an axis.

We were able to demonstrate the high regularity of the polymers prepared with the catalytic systems above described, through a detailed investigation of their crystalline structure.

In the present note we will relate on the results of a complete structural study concerning the isotactic polypropylene.

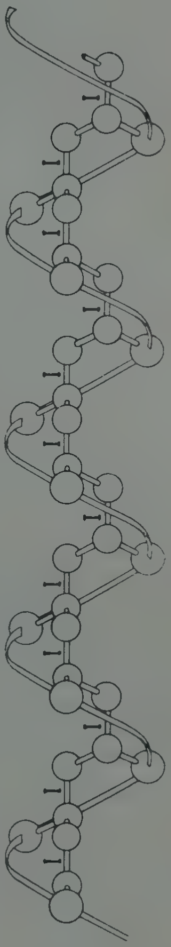

Fig. 3. – Conformation of an isotactic chain of polypropylene in the crystal state.

## 2. – Mode of crystallization of polypropylene.

The crystallinity, determined by a method performed in this Institute [5], of samples of polypropylene insoluble in boiling octane having a high sterical regularity, reaches high values for a polymer (until 85 %). These samples appear under the microscope, completely spherulitized (Fig. 5).

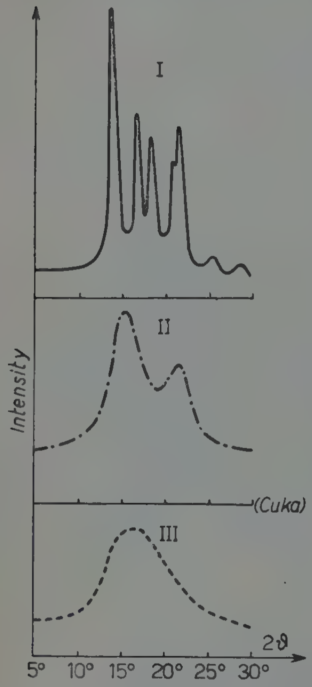

Fig. 4. – Comparison between the X-ray Geiger spectra (Cu, $K\alpha$) of a sample of crystalline isotactic polypropylene (I), a sample o fmesomorphous smectic isotactic polypropylene (II), a sample of amorphous atactic polypropylene (III).

Each spherulite, in analogy with the results obtained by other authors for many polymers, seems to be formed by small fibrils which irradiate themselves from the spherulite center. The cohesion among these fibrils is lower than within the fibrils, and the studies we have performed by X-ray diffraction [6], show that these fibrils are composed by crystal aggregates, all having the *a* axis (see paragraph on unit cell dimensions) parallel to the spherulite radius. The *a* axis should be thus coincident with the direction of the highest growing rate and in fact it corresponds to the shortest periodicity of the crystal in a direction different from that of the chain axis (*c*).

It is again the *a* axis which happens to be oriented along the axis of extruded, non stretched, filaments [6].

It is interesting to observe that if a sample of isotactic polypropylene is melted and then suddenly cooled in water, it gives an X-ray photograph different from the normal one. It has been assumed by us that a different modification of the polymer, with smectic character is reached; in fact the chains have still a threefold screw conformation as shown by the infrared spectrum, but a disorder exists in the packing of the chains perpendicularly to their axes (Fig. 4) [7].

## 3. – Stereoblock polymers.

The synthesis of isotactic polymers having a high crystallinity degree is generally accompanied by the formation of a certain amount of atactic polymers and of polymers having, in respect of isotactic polymers, lower degree

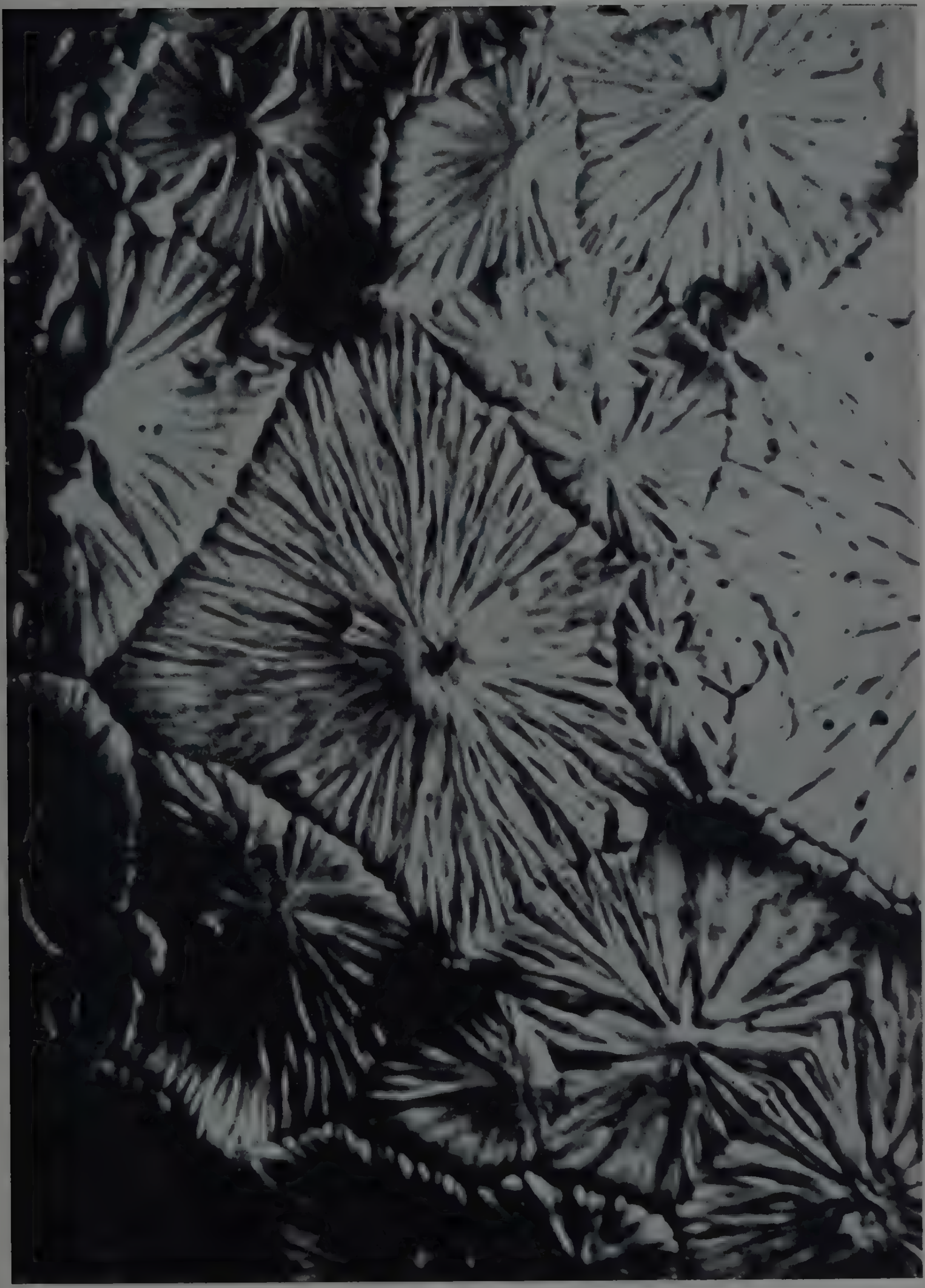

Fig. 5. – Film of polypropylene showing spherulites under the microscope (×100).

of crystallinity, greater solubility into hydrocarbon solvents and lower melting point [8, 9] (Fig. 6).

In Fig. 7 there are shown some X-ray photographs of polymers extracted with different hydrocarbon solvents. The polymer crystallinity generally increases with the increase of its melting point.

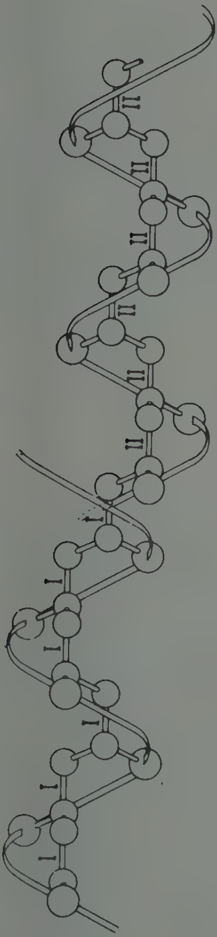

Fig. 6. – Possible model of a chain of stereoblock polypropylene.

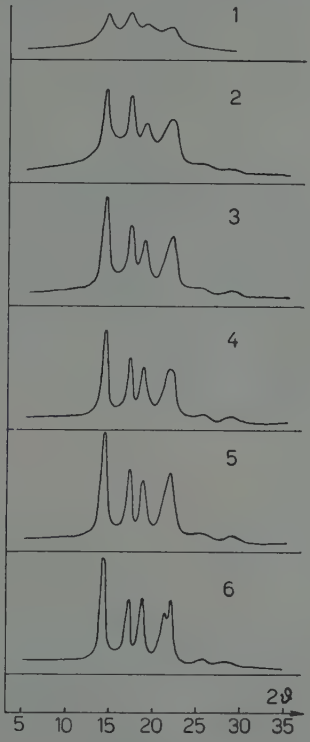

Fig. 7. – Geiger spectra (Cu, K$\alpha$) of stereoblock polymers of propylene. (1. Boiling pentane extracted fraction; Crystallinity: 27%; Melting point: 115 °C. 2. Boiling hexane extracted fraction; Cryst. 36%; M.P. 130 °C. 3. Boiling heptane extracted fraction: Cryst. 52%; M.P. 160 °C. 4. Boiling 2-ethylhexane extracted fraction: Cryst. 62%; M.P. 170 °C. 5. Boiling octane extracted fraction: Cryst. 64%; M.P. 174 °C. 6. Octane non extractible fraction: Cryst. 66%; M.P. 175 °C).

This fact may be justified by assuming that these polymers have a less regular structure, *e.g.* more or less frequent inversions of the isotactic order exist along the chain.

Should we consider the stereoblock polymers as copolymers of monomeric units with a given configuration with a small number of monomeric units having reversed configuration, we could expect that the melting point decreases. In a first approximation and for low $n$ values [9], where $n$ is the fraction of wrong monomeric units along the chain, it results:

$$T^0 - T = \frac{RT^0T}{\Delta H_{\text{u.m.}}} \ln(1-n) ,$$

where $T^\circ = 448°$ K, $T$ the melting point of the considered stereoblock sample, $\Delta H_{\text{u.m.}}$ the melting heat for monomeric unit (2400 cal) [10]. An increase of the solubility and a decrease of the crystallinity correspond to a decrease of the melting point, which may be determined, like crystallinity, by roentgenographic methods [5]. The formation of stereoblock polymers may be also connected with chain transfer processes [11]. It can be shown that an equation like the one previously proposed for the lowering of the melting point would still hold.

## 4. – Unit cell.

The determination of the unit cell was effected directly from fiber photographs taken from a specimen having a high isotacticity degree, with the methods of the reciprocal lattice [12].

The identity period along the axis of the chain results to be $(6.50 \pm 0.05)$ Å. The reciprocal lattice net of the equatorial reflections is rectangular with axes $a^* = 0.1524$ and $b^* = 0.0477$ (in $1/d$ units). The $hk0$ reflections with $h+k = 2n+1$ are systematically absent. This immediately suggests an orthorhombic or monoclinic symmetry for the unit cell and a centred unit cell, at least in projection on the $a$-$b$ plane, is expected. Then we also tried to index the reflections for which $l$ is different from zero. The indexing does not seem possible on the basis of an orthorhombic unit cell, *e.g.* with interaxial angles all measuring 90°, since there are few coincidences between the $\xi$ values of reflections belonging to different layer lines [13]. In fact, assuming that $c^*$ is inclined by 80°40′ on the $a^*$ axis, it is possible to index all $(hkl)$ reflections. The values of the unit cell constants are:

$$a = (6.65 \pm 0.05)\ \text{Å} ,$$

$$b = (20.96 \pm 0.15)\ \text{Å} ,$$

$$c = (6.50 \pm 0.05)\ \text{Å} ,$$

$$\beta = 99°\,20' \pm 1° .$$

Only $hkl$ reflections with $h+k=2n$ are present; this confirms that the whole crystal lattice is centered. Possible space groups are at this point $C2$, $Cm$, $Cc$, $C2/m$, $C2/c$.

The lack of $h0l$ reflections with $l=2n+1$ enables us to retain the space group $C2/c$ or its subgroup $Cc$ as the most probable space groups.

The $C2$ space group may be rejected also on the basis of the fact (less probable) that it does not allow the presence of enantiomorphous macromolecules in the unit cell.

In the unit cell 12 monomeric units are contained ($d_{\text{calc}} = 0{,}936$, $d_{\text{exp}} = 0.92$) and therefore four chain portions containing 3 monomeric units are present. The $Cc$ space group has just 4 general positions while the equivalent general positions of the $C2/c$ space group are 8; thus, unless a phenomenon of statistical vicariance is assumed, the most probable space group is the $Cc$ space group.

## 5. – Structural considerations.

The independent structural unit of the crystal is formed, as we have seen above, by a portion of chain containing three monomeric units.

The most probable way in which the three monomeric units repeat themselves so that they result equivalent in respect of the chain axis, is that of a helix [14]. By this assumption supported by many considerations [15], the shape of the chain remains determined by its repetition period (6.5 Å) and by the necessity of respecting known values of angles and distances between carbon atoms (Fig. 8). The found shape of the chain satisfies also the principle of the staggered simple bonds [14]. Having known the conformation of the chain, we tried the possible ways of packing according to the $Cc$ space group, so that the distances between the neighbouring carbon atoms of different macromolecules be always higher then 4 Å, as indicated by literature data concerning the structure of low molecular weight compounds [14].

Considering that the $Cc$ space group is: *a*) a centered space group; *b*) it shows symmetry planes with translation parallel to the axis of the chain in $y=0$, $y=\frac{1}{2}$, the most probable model results the one

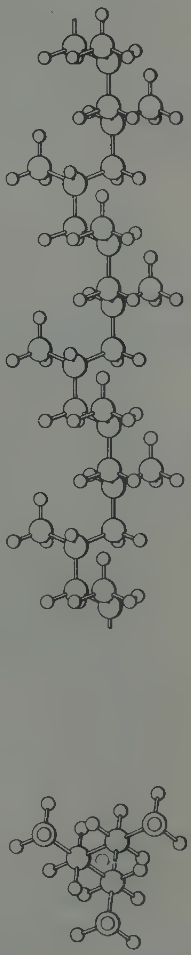

Fig. 8. – Conformation of a macromolecule of polypropylene (side and end views).

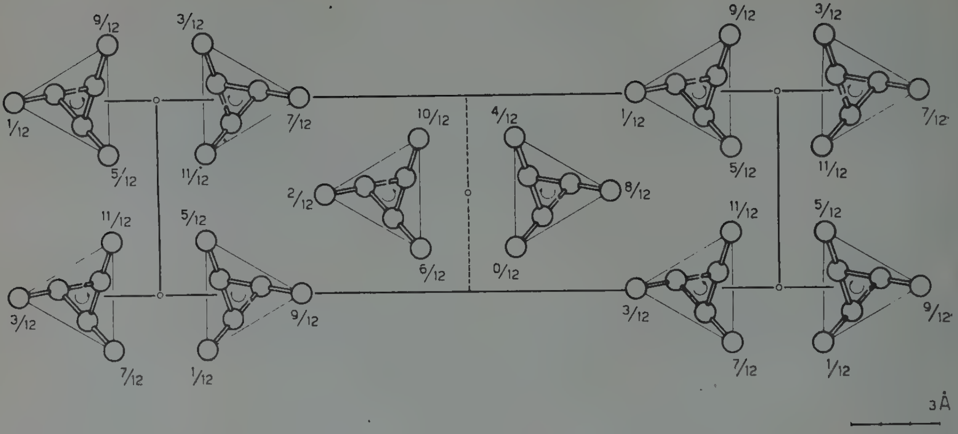

Fig. 9. – Projection on (001) of the structure of polypropylene for the *Cc* space group.

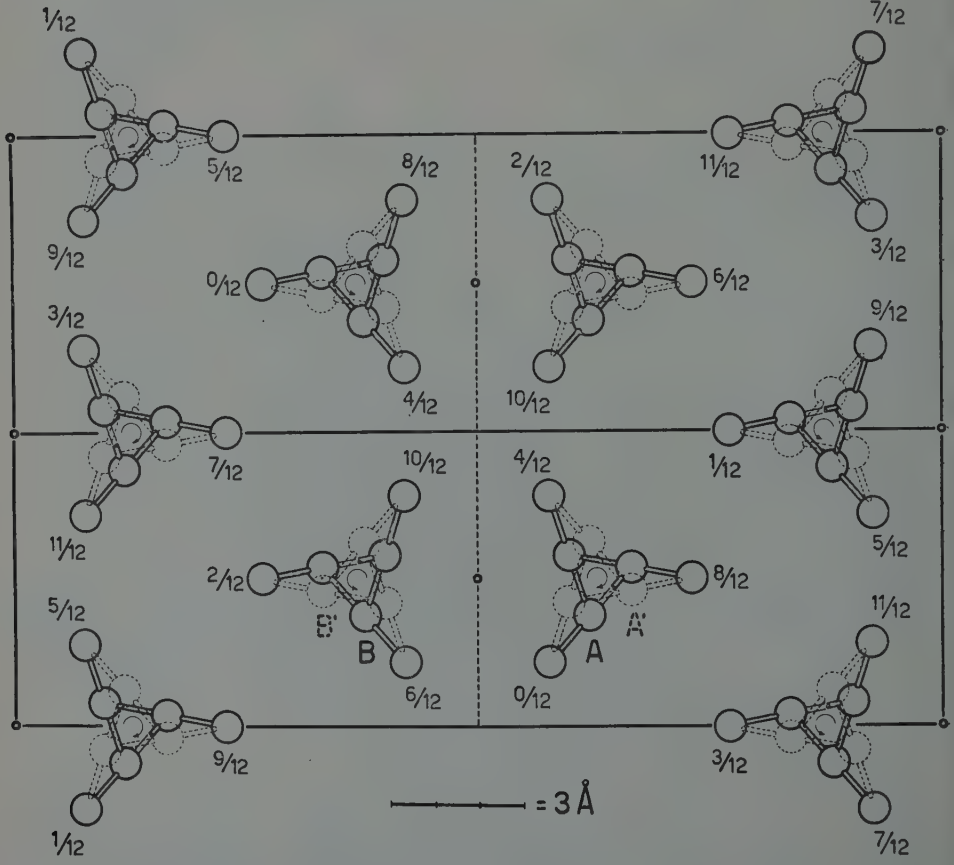

Fig. 10. – Projection on (001) of the structure of polypropylene for the *C*2/*c* space group.

sketched in Fig. 9. The contact distances between methyl groups of different molecules are, according to this model, all higher than 4.2 Å, while the distances between methyl and methylenic groups are all higher than 4.0 Å.

It is interesting to note at this point that the packing results good even if one substitutes an up molecule (full drawn in Fig. 9) with an isomorphous molecule, centrosymmetric in respect of the molecule which lies in front of it and therefore with the methyl group turned down (dashed in Fig. 9).

Should one assume that in each site isomorphous anticlined macromolecules can statistically be substituted, the new situation, that cannot be excluded on the basis of the contacts, corresponds to the *C*2/*c* space group of which *Cc* is a subgroup (Fig. 10).

Therefore in the following calculations even the possibility was taken into consideration that the space group is *C*2/*c*, taking account also of the fact that phenomena of statistical vicariance were previously observed in other polymers [16].

## 6. – Calculation of the structure.

The results of the calculation plotted in Table II have been obtained with the co-ordinates of the atoms supplied in Table I. They correspond to a shape of the chain in which the distances between singly linked carbon atoms have been assumed as equal to 1.54 Å, the angle C—C—C along the chain, inferable directly from the identity period, is of 114°, the two angles $CH_3$—C—C have been assumed as equal to 110°.

TABLE I. – *Co-ordinates of the independent structural unit of polypropylene.*

| Carbon atoms | Co-ordinates of the atoms in the unit cell (Sp. Gr. C 2/*c*) | | |
|---|---|---|---|
| | *x* | *y* | *z* |
| $C_1$ | .709 | .075 | .035 |
| $C_2$ | .924 | .100 | .151 |
| $C_3$ | .924 | .100 | .388 |
| $C_4$ | .290 | .075 | .465 |
| $C_5$ | .121 | .119 | .519 |
| $C_6$ | .121 | .119 | .756 |
| $C_7$ | .000 | .233 | .750 |
| $C_8$ | .967 | .164 | .826 |
| $C_9$ | .967 | .164 | .063 |

This last position leads to a slight displacement from the coplanarity of

TABLE II. – *Comparison between the observed and calculated structure factors of polypropylene.* The $F_0$ values correspond to the square root of the total intensity diffracted by the general $(h\,k\,l)$ lattice plane after effecting the corrections for the usual angular factors. The temperature factor is $B=7.5\,\text{Å}^2$ for the $C2/c$ and $B=8.5\,\text{Å}^2$ for the $C/c$ space group. In order to take into account the different multiplicities of the reflections the $F(h\,0\,l)$ and $F(0\,k\,0)$ calculated structure factors were divided by $\sqrt{2}$.

| *h k l* | F₀. | F꜀. *C 2/c* | F꜀. *Cc* |
|---|---|---|---|
| 0 2 0 | — | <1 | <1 |
| 1 1 0 | 55 | 62 | 61 |
| 0 4 0 | 54 | 55 | 54 |
| 1 3 0 | 64 | 61 | 60 |
| 1 5 0<br>0 6 0 | 35 | 30 | 30 |
| 2 0 0 | 18 | 19 | 19 |
| 2 2 0 | 34 | 29 | 28 |
| 2 4 0 | — | 6 | 6 |
| 1 7 0 | 12 | 11 | 13 |
| 0 8 0 | 3 | 5 | 5 |
| 2 6 0 | 10 | 14 | 14 |
| 1 9 0<br>3 1 0 | 15 | 17 | 19 |
| 0 10 0 | — | 5 | 5 |
| 3 3 0 | — | 7 | 9 |
| 2 8 0 | 12 | 12 | 16 |
| 3 5 0 | 3 | 6 | 6 |
| 1 11 0 | — | 2 | 7 |
| 2 10 0<br>3 7 0 | 9 | 9 | 9 |
| 0 12 0 | 10 | 9 | 9 |
| 4 0 0<br>4 2 0 | 4 | 6 | 11 |
| 3 9 0<br>1 13 0<br>4 4 0 | 12 | 13 | 15 |
| 2 12 0 | — | 3 | 11 |
| 0 14 0<br>4 6 0 | 7 | 4 | 3 |
| 3 11 0 | — | 3 | 8 |
| 4 8 0 | 7 | 8 | 7 |
| 1 15 0<br>2 14 0 | 16 | 16 | 14 |
| 0 16 0<br>5 1 0 | 12 | 9 | 10 |
| 3 13 0<br>4 10 0<br>5 3 0 | 13 | 13 | 14 |
| 5 5 0 | 17 | 12 | 11 |

| *h k l* | F₀. | F꜀. *C 2/c* | F꜀. *Cc* |
|---|---|---|---|
| 2 16 0 | — | 6 | 8 |
| 1 17 0 | — | 5 | 5 |
| 5 7 0<br>4 12 0 | 9 | 9 | 9 |
| 0 18 0<br>5 9 0 | 7 | 5 | 4 |
| 4 14 0 | — | 3 | 4 |
| 2 18 0<br>6 0 0<br>1 19 0 | — | 7 | 7 |
| 5 11 0 | — | 3 | 3 |
| 3 17 0 | — | <1 | 2 |
| 0 2 1 | — | 1 | 2 |
| 1 1 $\bar{1}$ | 3 | 4 | 5 |
| 1 1 1 | 47 | 41 | 46 |
| 1 3 $\bar{1}$<br>0 4 1 | 67 | 62 | 69 |
| 1 3 1 | 12 | 12 | 14 |
| 1 5 $\bar{1}$ | 7 | 8 | 10 |
| 0 6 1 | — | 2 | 10 |
| 2 2 $\bar{1}$<br>1 5 1 | 6 | 9 | 20 |
| 2 4 $\bar{1}$<br>2 2 1 | 16 | 8 | 36 |
| 1 7 $\bar{1}$ | 14 | 7 | 30 |
| 1 7 1 | — | 4 | 5 |
| 0 8 1<br>2 4 1 | 18 | 21 | 25 |
| 2 6 $\bar{1}$ | 20 | 18 | 22 |
| 3 1 $\bar{1}$<br>2 6 1 | 13 | 1 | 12 |
| 1 9 $\bar{1}$<br>3 3 $\bar{1}$ | 21 | 22 | 23 |
| 1 9 1 | — | 2 | 2 |
| 2 8 $\bar{1}$<br>0 10 1<br>3 1 1 | 17 | 20 | 29 |
| 3 5 $\bar{1}$<br>3 3 1 | 15 | 24 | 28 |
| 2 8 1 | — | 7 | 7 |

TABLE II (*continued*).

| *h k l* | $F_{o.}$ | $F_{c.}$ *C* 2/*c* | $F_{c.}$ *Cc* | *h k l* | $F_{o.}$ | $F_{c.}$ *C* 2/*c* | $F_{c.}$ *Cc* |
|---|---|---|---|---|---|---|---|
| 3 5 1<br>1 11 $\bar{1}$ | 9 | 8 | 19 | 4 4 $\bar{1}$ | — | 6 | 8 |
| 3 7 $\bar{1}$ | — | < 1 | 13 | 1 13 $\bar{1}$<br>2 12 $\bar{1}$<br>4 2 1 | 16 | 13 | 16 |
| 1 11 1<br>2 10 $\bar{1}$ | 10 | 13 | 16 | 1 13 1 | — | 5 | 6 |
| 0 12 1 | — | 8 | 8 | 3 9 1 | — | 9 | 8 |
| 2 10 1<br>3 7 1<br>4 2 $\bar{1}$ | 11 | 14 | 15 | 4 6 $\bar{1}$ | — | 3 | 3 |
| | | | | 2 12 1 | — | 5 | 6 |
| | | | | 4 4 1 | — | 1 | 2 |
| 3 9 $\bar{1}$ | — | 5 | 6 | | | | |

the methyl group in respect of one of the three planes in which, four by four, the carbon atoms of the chain are lying.

We shall try to bring experimental evidence which favours this model. The structure factor, in the *C*2/*c* space group, is given by the relation (neglecting the hydrogen atoms in the calculation):

$$A = \sum 4f_c \cos^2 2\pi \frac{h+k}{4} \cos 2\pi \left(hx + lz + \frac{l}{4}\right) \cos 2\pi \left(ky - \frac{l}{4}\right),$$

whereas for the *Cc* space group it is given by the relationship [17]:

$$A = \sum 4f_c \cos^2 2\pi \frac{h+k}{4} \cos 2\pi \left(hx + lz + \frac{l}{4}\right) \cos 2\pi \left(ky - \frac{l}{4}\right),$$

$$B = \sum 4f_c \cos^2 2\pi \frac{h+k}{4} \sin 2\pi \left(hx + lz + \frac{l}{4}\right) \cos 2\pi \left(ky - \frac{l}{4}\right).$$

The structure factors calculated according to the *C*2/*c* space group are thus all averagely lower than those calculated according to the *Cc* space group. This corresponds to the fact that, in structures showing statistical disorder, the mean diffracted intensity by lattice planes is lower than the one diffracted by ordered structures [18].

The mean value of the structure factor is given, in fact, in a non-statistical structure having $N$ equal atoms per unit cell, by the relationship:

$$\bar{I} = \sum^{N} f_i^2 = Nf^2 ,$$

where $f$ is the scattering factor of the considered atom. A statistical structure with $N$ equal atoms per unit cell, which are able to take two different positions at random, will diffract as if it had $2N$ equal atoms per unit cell, with a scattering factor $\frac{1}{2}f$. Provided that such different positions are not coincident with the possible ones of other atoms, the average scattered intensity is given by

$$\bar{I} = \sum^{2N} (\tfrac{1}{2}f_i)^2 = \tfrac{1}{2}Nf^2 .$$

In the case of polypropylene, where the methyl groups of molecules vicariant according to $C2/c$ would always have the same position, we have:

$$\bar{I} = \tfrac{2}{3}Nf^2 .$$

In fact, the values calculated for the $(hk0)$ reflections are very similar for the two space groups, but the values calculated for the $(hk1)$ reflections are actually much higher for the $Cc$ space group than for the $C2/c$ space group.

From Table II it may be seen that a better agreement with the experimental values can be obtained for the structure factors calculated according to the $C2/c$ space group. However, the course of the values calculated for the $Cc$ space group is very similar to that calculated for the $C2/c$ space group and, whereas the two calculated values are very different, the observed structure factor often has an intermediate value.

A choice between the two space groups results therefore rather difficult. That probably corresponds to the true situation of the crystal. We believe that the crystalline structure of polypropylene just locally corresponds to the $Cc$ space group, *i. e.*, each single crystal should be constituted by an aggregate of small blocks, anticlined among themselves, of isoclined macromolecules. Thus, in each block, the structure corresponds to the situation outlined in

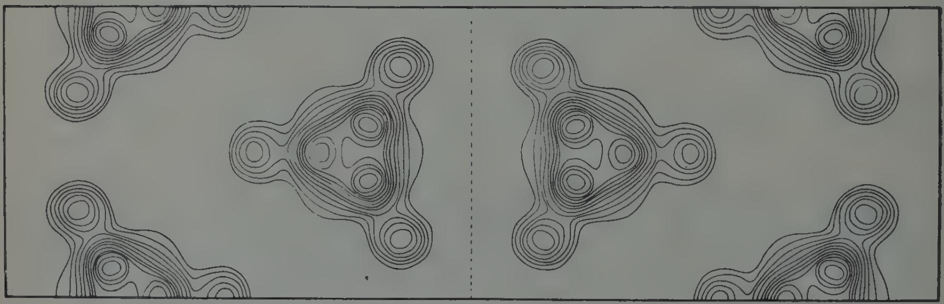

Fig. 11. – Electron density projection on (001) of polypropylene calculated according to the $C2/c$ space group. Contours are drawn every $0.5e/\text{Å}^2$. The first line corresponds to the $2e/\text{Å}^2$ level.

Fig. 9, that is to the *Cc* space group. If the equatorial periodicities are maintained unaltered at the jointment planes between the anticlined blocks, in a generical site of a composite crystal it should be however possible to find almost statistically macromolecules anticlined among themselves. The smaller are the blocks of macromolecules isoclined among them, the more the experimental structure factor disagrees with that calculated for the *Cc* space group and agrees with the one that may be calculated for the *C2/c* space group.

A Fourier synthesis of the electronic density was performed along *c* for this group and enabled us to fix within 0.05 Å the co-ordinates of the atoms.

These co-ordinates are very nearly those given in Table I for the model illustrated at the beginning of this paragraph.

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SUPPLEMENTO AL VOLUME XV, SERIE X
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# Crystal Structure of Isotactic Poly-alpha-Butene.

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(ricevuto il 26 Giugno 1959).

In these last years crystalline polymers of alpha-olefins were synthesized in the laboratory of Industrial Chemistry of the Milan Polytechnic. Many of them, such as polypropylene and poly-alpha-butene, are expected to increase their importance because of the excellent physical properties they possess, the low cost and the many foreseeable industrial applications. Their structure has been, therefore, the object of a broad investigation.

We shall refer, in this paper, on the results of our structure studies related to poly-alpha-butene. Preliminary results are outlined in a preceding letter to the Editor [1] of *Makromolekulare Chemie.*

*Unit cell.* – The isotactic polymers of alpha-butene insoluble in ethyl ether prepared by the methods of stereospecific catalysis of co-ordinated anionic type ($TiCl_3 + Al(C_2H_5)_3$) have a degree of crystallinity measured by X-ray methods [2] of the order of 60%.

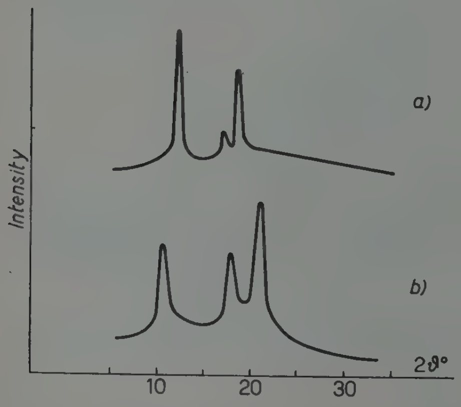

Fig. 1. – Powder spectra of crystalline poly-alpha-butene registered with a Geiger counter (Cu, K$\alpha$): *a*) modification 2; *b*) modification 1.

Isotactic poly-alpha-butene shows two crystalline modifications [3]. One of them (modification 1), whose structure is the object of this paper, appears the most stable one at room temperature; the other one (modification 2) is that occurring first, at the moment of crystallization, both from the melt and from solutions. The modification 2 is able to evolve in the most stable modification, at

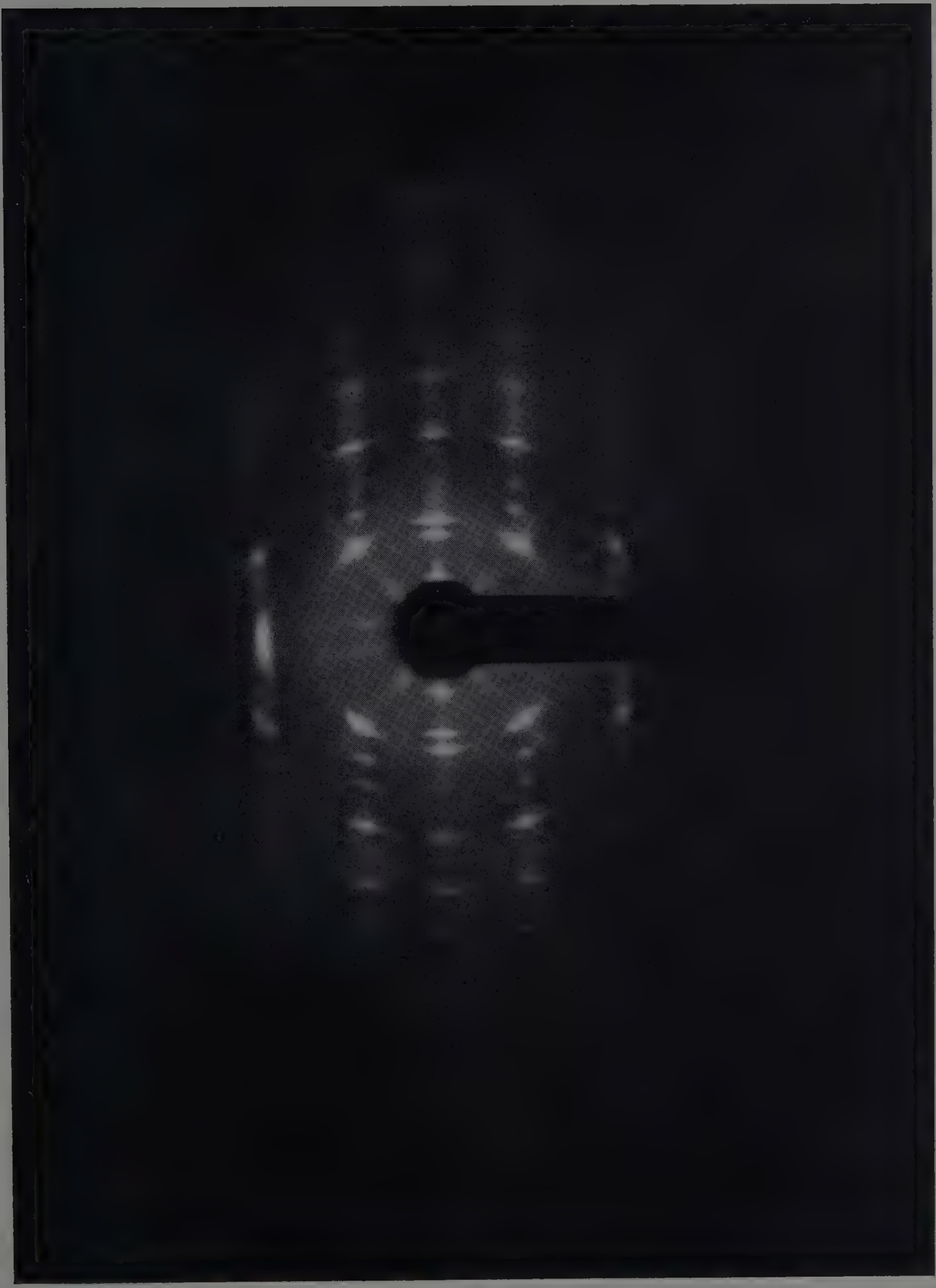

Fig. 2. – Fiber photograph of poly-alpha-butene.

a more or less high rate, according to the preceding history of the sample and to the thermal or mechanical treatments it undergoes (pressure, unidirectional stretching). The two forms are characterized by a different identity period and, thus, by a different symmetry of the chain. In Fig. 1 is shown, as an example, the X-ray powder spectrum, registered with a Geiger counter, of a sample of poly-alpha-butene cooled from the melted state without pressure *a*), (modification 2), and the powder spectrum of the same specimen after submitting it, at room temperature, to a pressure of 100 atm, for a few seconds *b*), (modification 1).

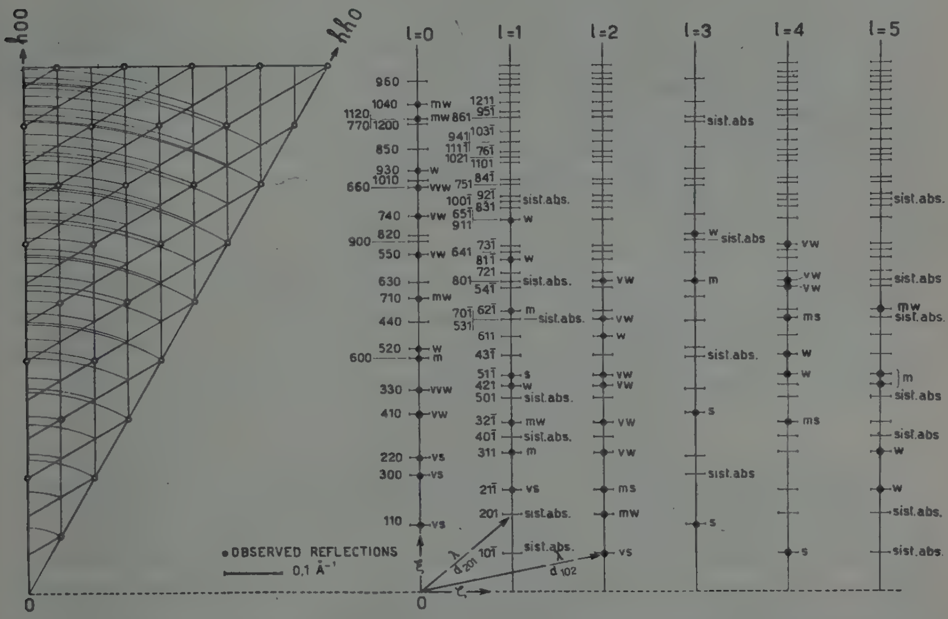

Fig. 3. – Reciprocal lattice of poly-alpha-butene (interpretation of an electron diffraction spectrum of a drawn film of polymer).

In the present study, only the most stable modification will be considered.

Fiber spectra have been taken in a cylindrical camera by Cu, K α radiation. The identity period along the axis of the chain is $6.50 \pm 0.05$ Å.

The photographs show numerous, sharp and, therefore, well resolved reflections (Fig. 2).

It was possible to index all reflections by the reciprocal lattice method (Fig. 3), on the basis of a rhombohedral unit cell whose identity period $a$, referred to hexagonal axes, is $(17.7 \pm 0.1)$ Å. The $(hkl)$ reflections are present only when $-h+k+l=3n$.

The choice of the possible space groups, from the systematic absence of $(h0l)$ reflections with $l=2n+1$, is restricted to $R3c$ and $R\bar{3}c$ groups.

The experimental density is that expected if 18 monomeric units are present per unit cell. The $R3c$ space group has just 18 equivalent points in general position, whilst 36 are those foreseen for the $R\bar{3}c$ space group. The two space groups differ one from another according to the presence or to the absence of symmetry centers.

The $R\bar{3}c$ space group may occur only if chains, with different polar orientation, (anticlined), isomorphous to each other [4] are able to vicariate in a statistical way around the same threefold screw axis, whereas the $R3c$ space group is possible only if the chains are able to arrange themselves in the crystal lattice, all having the same polar orientation (isoclined).

Anyway, only chains with threefold helical symmetry are allowed to be present in the unit cell; each right-handed polymer chain is surrounded by three left-handed chains and viceversa.

The monomeric units following one to another along the threefold helix must obviously have the same sterical conformation.

We have demonstrated that a regular helix type succession in a crystalline vinyl polymer is possible only when the polymer is isotactic [5, 6].

*Structure.* The shape of the main chain of the polymer can be deduced from its threefold helical symmetry and from the knowledge of accepted data, concerning angles and distances between carbon-carbon single bonds. It corresponds to a succession of bonds alternately with trans and gauche conformations. The gauche conformations may be either right or left handed, thus generating, following the terminology introduced by BUNN, $(AB)_3$ or $(AC)_3$ enantiomorphous helical chains [7]. The angle between carbon-carbon bonds of the main chain, which may be deduced directly from the value of the identity period $c$, differs remarkably from the tetrahedral value and reaches 114°.

The position of the ethyl side group was foreseen in such a way as to satisfy the principle of staggered bonds, and in order to realize suitable Van der Waals distances between different atoms of the same chain.

On the basis of these principles the shape of the chain of poly-alpha-butene remains univocally determined and is shown in Fig. 4.

The problem of determining the way of packing of the macromolecules between themselves has been faced by us both (I) through the consideration of significantly intense $(hk0)$ reflections and (II) taking into account the principle that Van der Waals contacts between neighbouring carbon atoms of different chains should not be lower than 4 Å, in accordance with the current data of the most recent literature [8].

An outstanding equatorial reflection is that observed at a Bragg distance $d=1.27$ Å. It corresponds, however, to the possible superposition of two reflections, the (11 2 0) and the ( 7 7 0) ones, which cannot be distinguished in a fiber diagram.

Making a fiber undergo a strong pressure in a direction normal to its axis (crushing it under the wheels of a tramway car), it was possible to achieve a further orientation of the crystallites.

The *a* axis becomes oriented perpendicularly both to the direction of the fiber axis *c* and to the direction along which the pressure was applied. The double orientation is so good that the X-ray spectrum given by the sample resembles that given by a single crystal. Thus, it has been possible to us to assign the (7 7 0) indices to the outstanding reflection with $d = 1.27$ Å.

The (7 7 0) structure factor (which has the same analytical expression for the possible space groups $R3c$ or $R\bar{3}c$) is so high, that it demands that all the atoms of the independent structural unit scatter nearly in phase. The (7 7 0) structure-factor graph is shown in Fig. 5 [9]. The molecule, keeping into consideration also the Van der Waals contacts with the neighbouring molecules, remains compelled to assume the position drawn in the graph itself. It is worth noticing, at this point, that the position held in the space by the independent structural unit is such that the Van der Waals contacts between different molecules are good even if we assume that statistical vicariance of up and down molecules, around the same threefold screw axis, occurs, as needed by the $R\bar{3}c$ space group. In fact, after suitably choosing the origin of $z$ coordinates for the independent structural unit, values of Van der Waals contacts between neighbouring molecules, packed according to the $R\bar{3}c$ space group, are obtained, all of them being greater than 4 Å and quite similar to those realized also in the $R3c$ space group (Fig. 6). For the latter space group the mode of packing results independent of the choice of the origin along $c$.

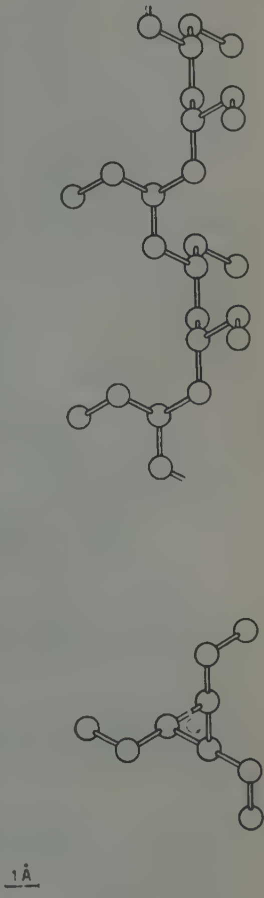

Fig. 4. – Conformation of poly-alpha-butene macromolecule in the crystalline state.

As shown in Fig. 7 if the space group is $R3c$, the macromolecules are isoclined and each of them is surrounded by three enantiomorphous macromolecules and viceversa. On the other hand, should the space group be $R\bar{3}c$ (Fig. 8) each macromolecule is still surrounded by three enantiomorphous molecules and, furthermore, reciprocally anticlined macromolecules may vicariate in a statistical way around each threefold screw axis. The foreseeable statistical vicariance of anticlined macromolecules removes any polarity from the $c$ axis.

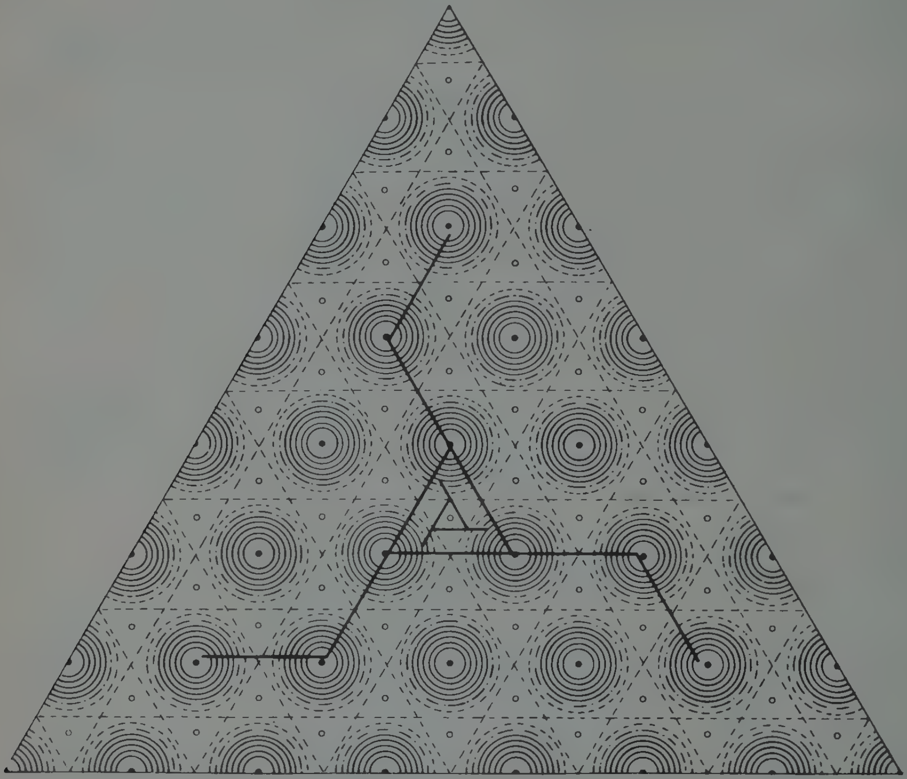

Fig. 5. – (7 7 0) structure factor graph of poly-alpha-butene, showing the position of the macromolecule (contours drawn at regular intervals: positive lines ———, zero lines —·—·—·—, negative lines – – – – –).

A preliminary calculation of the structure factors was performed for both space groups.

The agreement between calculated and observed structure-factors results much better for the centrosymmetrical space group $R\bar{3}c$.

It is possible to explain this result by the assumption that the single crystals of the polymer are composed of small blocks, each of them being formed by reciprocally isoclined macromolecules, and thus with a symmetry corresponding to the $R3c$ space group. These blocks, closely superposed in an anticlined way, would simulate, as far as the global diffraction effects are concerned, the statistical situation foreseeable on the basis of the $R\bar{3}c$ space group. A choice between the two space groups is thus very difficult and would be critically determined by the dimensions of the blocks.

By the signs resulting from the calculation of the structure factors of ($h\,k\,0$) reflections it was possible to obtain a Fourier projection of the electron density (Fig. 9) which, though on one side confirming the substantial correctness of the assumed structure, on the other hand pointed out the fact that the

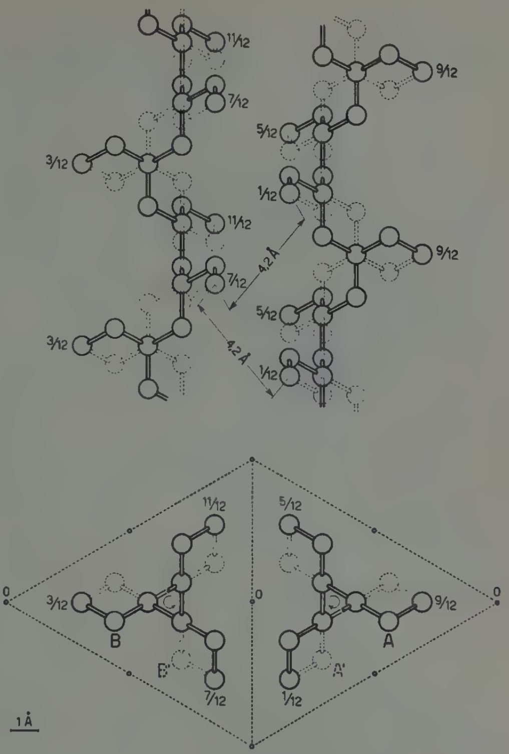

Fig. 6. – Model showing isosterism of anticlined isomorphous macromolecules of poly-alpha-butene in the crystal.

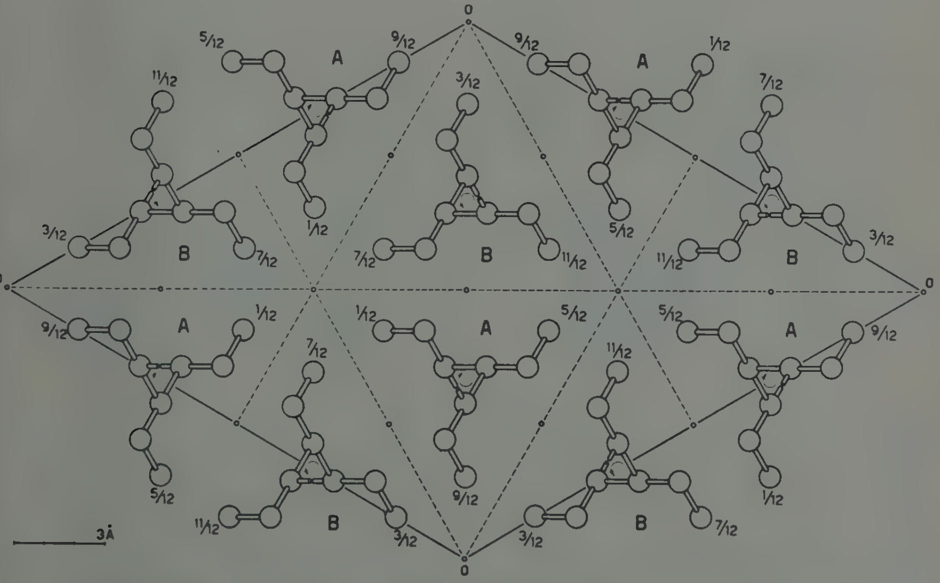

Fig. 7. – Projection of the structure of poly-alpha-butene on (001) for the $R3c$ space group.

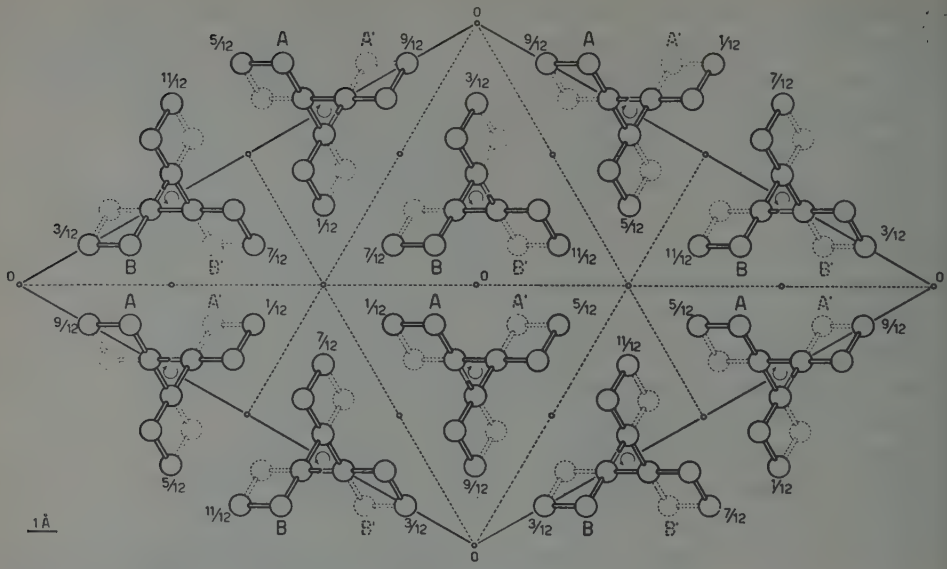

Fig. 8. – Projection of the structure of poly-alpha-butene on (001) for the $R\bar{3}c$ space group.

methylenic carbon atom of the ethyl group ($C_3$ in Fig. 10) does not lay on the same plane on which 4 by 4 the carbon atoms of the main chain (say for instance, as in Fig. 10, $C_{1a}\,C_{2a}\,C_1\,C_2$) lay along the helix.

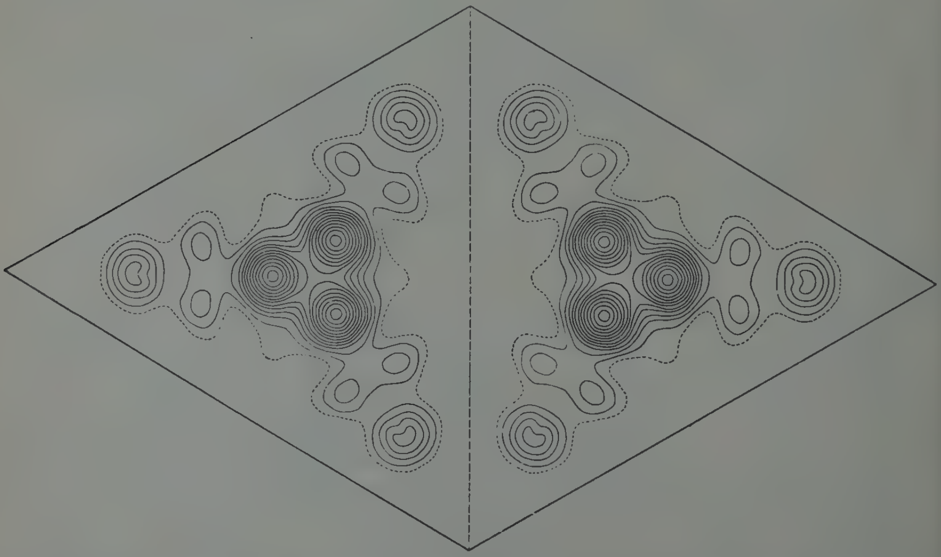

Fig. 9. – Poly-alpha-butene electron density projection on (001), calculated according to the $R\bar{3}c$ space group (contours at intervals of $0.5e$ Å$^2$, the broken line is the $2e$/Å$^2$ level).

In the original model, on the contrary, the carbon atoms were arranged staggered on the same plane 5 by 5 (Fig. 4).

In fact, as it comes out from Fig. 10, should one assume that the $C_1\widehat{C_2}C_{1b}$ and $C_2\widehat{C_1}C_{2a}$ angles are 114° and that the $C_1\widehat{C_2}C_3$ and $C_{1b}\widehat{C_2}C_3$ angles cannot go down to values below the tetrahedral ones (109° 28′) the discussed displacement can be justified at once (Fig. 11).

This displacement will generally occur in each isotactic polymer with threefold helix, given that the $C_1\widehat{C_2}C_{1b}$ and $C_2\widehat{C_1}C_{2a}$ angles, Fig. 10, along the chain, which may be calculated from the observed identity periods, overcome in any case the tetrahedral values.

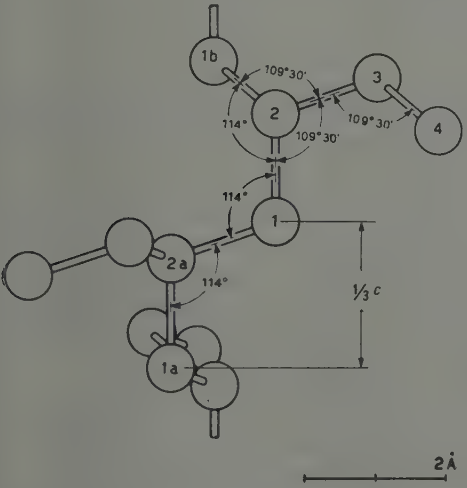

Fig. 10. – Model of the independent structural unit of poly-alpha-butene showing angles and distances between atoms (C—C = 1.54 Å).

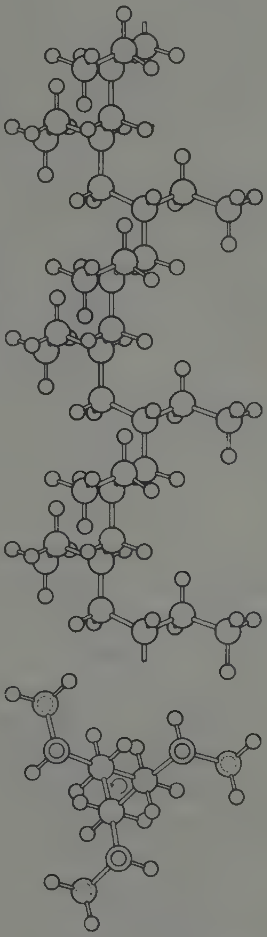

Fig. 11. – Actual conformation of the poly-alpha-butene macromolecule in the crystalline state (side and end views).

A recalculation of the structure factors was effected and showed a remarkable improvement in the accordance.

The best atomic co-ordinates found by us are plotted in Table I, and the results of the calculation, including also hydrogen atoms, supposing the temperature factor to be $B = 8.9$ Å² are plotted in Table II. The introduction

TABLE I. – *Co-ordinates of the atoms of the independent structural unit.* (The atoms are marked according to Fig. 10; the hydrogen atoms index refers to the carbon atom to which they are linked).

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| $C_1$ | 0.288 | 0.288 | 0.015 |
| $C_2$ | 0.288 | 0.288 | 0.250 |
| $C_3$ | 0.232 | 0.192 | 0.330 |
| $C_4$ | 0.136 | 0.143 | 0.250 |
| $H_1$ | 0.322 | 0.254 | 0.960 |
| $H_{1'}$ | 0.220 | 0.254 | 0.960 |
| $H_2$ | 0.253 | 0.320 | 0.304 |
| $H_3$ | 0.233 | 0.191 | 0.496 |
| $H_{3'}$ | 0.265 | 0.157 | 0.271 |
| $H_4$ | 0.136 | 0.143 | 0.082 |
| $H_{4'}$ | 0.101 | 0.176 | 0.304 |
| $H_{4''}$ | 0.101 | 0.074 | 0.304 |

into the calculation of the contribution of the hydrogen atoms caused a true improvement for some reflections (*e.g.* (330), (321), $(40\bar{2})$, (502)), whose calculated structure factors deviated a little from the observed value.

The fact that the improvement introduced by the consideration of hydrogen atoms is appreciable only for low angle reflections may be readily understood, because of the very low diffracting power of hydrogen at high $2\vartheta$ values. Moreover, the improvement is expected to be appreciable only when almost all hydrogen atoms are in phase coincidence one with another. The reliability index calculated for observed and non-observed reflections up to $d = 1,0$ Å for 0, 1, 2, 3 layer lines results to be 0.23 and is one of the best values, until now obtained, for the structure of a polymer. The corresponding Fourier projection of the content of the unit cell, already shown in Fig. 9, presents different maxima of relative weight $2 : \frac{1}{2} : 1$ in respect of the number of atoms which are truly projected herein. In Table III also the values of the structure factors calculated for the $R3c$ space group for the same independent unit are given for comparison with the observed ones. According to our opinion, the results are less good ($R = 0.32$).

The structure of poly-alpha-butene shows a remarkable analogy with that of polystyrene on one side and of polypropylene on the other.

In any case, the presence, at the same time, in the unit cell of enantiomorphous molecules is actuated by means of a glide plane with translation along $c$ (Fig. 12). In the case of poly-alpha-butene and polystyrene, the crystal shows also the threefold symmetry peculiar to the chain, contrary to poly-

TABLE II. – *Comparison between calculated and observed structure factors of poly-alpha-butene according to the $R\bar{3}c$ space group.*

The $F_0$ values correspond to the square root of the total intensity diffracted by the general $(h\,k\,l)$ lattice plane, after effecting the corrections for the usual angular factors. In order to take into account the different multiplicity of reflections, all the calculated structure factors except the $(h00)$, $(hh0)$ and $(h0l)$ ones, were multiplied by $\sqrt{2}$. The numbers into brackets are the values which the structure factors of non-observed reflections should assume if their intensity were one half of the lowest observed one. (Cu, K $\alpha$).

| *h k l* | 2 sin $\vartheta$ | $F_c$ | $F_o$ | *h k l* | 2 sin $\vartheta$ | $F_c$ | $F_o$ |
|---|---|---|---|---|---|---|---|
| 1 1 0 | 0.174 | − 69 | 92 | 4 2 $\bar{1}$ | 0.580 | − 18 | 15 |
| 3 0 0 | 0.301 | + 87 | 105 | 5 1 1 | 0.606 | + 67 | 70 |
| 2 2 0 | 0.347 | −110 | 127 | 4 3 1 | 0.654 | + 8 | (3) |
| 4 1 0 | 0.460 | − 14 | 13 | 6 1 $\bar{1}$ | 0.701 | − 2 | (4) |
| 3 3 0 | 0.521 | − 4 | (2) | 5 3 $\bar{1}$ | 0.741 | + 6 | (4) |
| 6 0 0 | 0.602 | + 33 | 40 | 6 2 1 | 0.761 | − 41 | 38 |
| 5 2 0 | 0.626 | − 24 | 23 | 5 4 1 | 0.818 | − 5 | (4) |
| 4 4 0 | 0.695 | + 1 | (3) | 7 2 $\bar{1}$ | 0.854 | + 1 | (4) |
| 7 1 0 | 0.758 | + 33 | 31 | 8 1 1 | 0.889 | + 37 | 38 |
| 6 3 0 | 0.796 | − 2 | (3) | 6 4 $\bar{1}$ | 0.905 | + 7 | (4) |
| 5 5 0 | 0.869 | − 20 | 17 | 7 3 1 | 0.922 | − 5 | (4) |
| 9 0 0 | 0.903 | − 2 | (3) | 6 5 1 |  | − 33 |  |
| 8 2 0 | 0.919 | + 1 | (3) |  | 0.985 | 33 | 28 |
| 7 4 0 | 0.967 | + 17 | 18 | 9 1 $\bar{1}$ |  | <+1 |  |
| 6 6 0 | 1.042 | − 14 | 16 | 8 3 $\bar{1}$ | 1.016 | + 1 | (5) |
| 10 1 0 | 1.057 | + 2 | (4) | 9 2 1 | 1.045 | — | (5) |
| 9 3 0 | 1.085 | − 22 | 21 | 7 5 $\bar{1}$ | 1.073 | + 1 | (5) |
| 8 5 0 | 1.140 | − 11 | 14 | 8 4 1 | 1.087 | + 22 | 19 |
| 12 0 0 | 1.204 | − 8 | (4) | 10 2 $\bar{1}$ | 1.140 | − 5 | (5) |
| 11 2 0 |  | − 2 |  | 7 6 1 | 1.155 | + 3 | (5) |
|  | 1.216 | 35 | 28 | 11 1 1 |  | + 9 |  |
| 7 7 0 |  | + 35 |  |  | 1.181 | 24 | 23 |
| 10 4 0 | 1.253 | + 14 | 17 | 9 4 $\bar{1}$ |  | − 22 |  |
| 9 6 0 | 1.311 | − 5 | (4) | 10 3 1 | 1.205 | + 6 | (5) |
| 13 1 0 | 1.357 | + 8 | <6 | 8 6 $\bar{1}$ | 1.242 | + 2 | (5) |
| 12 3 0 | 1.379 | − 1 | (4) | 9 5 1 | 1.254 | + 1 | (5) |
| 8 8 0 | 1.390 | − 3 | (4) | 12 1 $\bar{1}$ | 1.278 | + 11 | <9 |
| 11 5 0 | 1.422 | − 11 | 10 | 11 3 $\bar{1}$ | 1.301 | − 4 | (6) |
| 10 7 0 | 1.485 | + 8 | 6 | 8 7 1 | 1.325 |  | (6) |
| 15 0 0 | 1.504 | + 2 | (4) | 12 2 1 | 1.337 | − 1 | (6) |
| 14 2 0 | 1.515 | − 1 | (4) | 10 5 $\bar{1}$ | 1.347 | + 10 | 11 |
| 13 4 0 | 1.544 | + 1 | (4) | 11 4 1 | 1.369 | − 1 | (6) |
| 9 9 0 | 1.564 | − 5 | (4) | 9 7 $\bar{1}$ | 1.413 | + 1 | (6) |
|  |  |  |  | 10 6 1 | 1.424 | − 10 |  |
| 2 1 1 | 0.355 | +152 | 175 |  |  | 14 | 15 |
| 3 1 $\bar{1}$ | 0.432 | − 39 | 40 | 13 2 $\bar{1}$ | 1.434 | + 9 |  |
| 3 2 1 | 0.497 | + 32 | 22 | 12 4 1 | 1.466 | <+1 | (6) |

TABLE II (*continued*).

| $h\,k\,l$ | 2 sin ϑ | F$_c$ | F$_o$ |
|---|---|---|---|
| 14 1 1 | 1.477 | − 1 | (6) |
| 13 3 1 | | − 1 | |
| | 1.497 | 2 | (6) |
| 9 8 1 | | − 2 | |
| 11 6 $\bar{1}$ | 1.516 | + 3 | (6) |
| 12 5 1 | 1.536 | − 1 | (6) |
| 1 0 $\bar{2}$ | 0.481 | − 54 | not calc. |
| 2 0 2 | 0.512 | − 20 | 11 |
| 2 1 $\bar{2}$ | 0.540 | + 28 | 26 |
| 3 1 2 | 0.594 | + 17 | 12 |
| 4 0 $\bar{2}$ | 0.618 | + 12 | 8 |
| 3 2 $\bar{2}$ | 0.642 | + 12 | 14 |
| 5 0 2 | 0.688 | − 2 | (3) |
| 4 2 2 | 0.710 | + 21 | 17 |
| 5 1 $\bar{2}$ | 0.730 | − 12 | 15 |
| 4 3 $\bar{2}$ | 0.771 | + 3 | (3) |
| 6 7 2 | 0.809 | − 29 | 22 |
| 7 0 $\bar{2}$ | | + 1 | |
| | 0.845 | 17 | 15 |
| 5 3 2 | | + 17 | |
| 6 2 $\bar{2}$ | 0.863 | − 11 | 12 |
| 5 4 $\bar{2}$ | 0.914 | − 4 | (4) |
| 8 0 2 | 0.930 | − 20 | 22 |
| 7 2 2 | 0.946 | − 6 | (4) |
| 8 1 $\bar{2}$ | 0.978 | − 9 | < 7 |
| 6 4 2 | 0.993 | + 4 | (4) |
| 7 3 $\bar{2}$ | 1.020 | + 1 | (4) |
| 6 5 $\bar{2}$ | | + 11 | |
| | 1.066 | 13 | 14 |
| 9 1 2 | | + 7 | |
| 8 3 2 | 1.094 | + 5 | (5) |
| 10 0 $\bar{2}$ | 1.108 | − 1 | (5) |
| 9 2 $\bar{2}$ | 1.121 | + 1 | (5) |
| 7 5 2 | 1.148 | − 4 | |
| | | 10 | 8 |
| 8 4 $\bar{2}$ | 1.161 | + 9 | |
| 11 0 2 | 1.200 | < +1 | (5) |
| 10 2 2 | 1.212 | + 5 | < 8 |
| 7 6 $\bar{2}$ | 1.224 | − 6 | < 8 |
| 9 4 2 | | + 5 | |
| | 1.248 | 10 | 9 |
| 11 1 $\bar{2}$ | | + 8 | |
| 10 3 $\bar{2}$ | 1.273 | < +1 | (5) |
| 8 6 2 | 1.308 | − 9 | 10 |
| 9 5 $\bar{2}$ | 1.319 | − 4 | (5) |
| 12 1 2 | 1.350 | − 3 | (6) |
| 1 1 3 | | − 28 | |
| | 0.731 | 39 | not calc. |
| 1 1 $\bar{3}$ | | + 28 | |
| 2 2 3 | | − 7 | |
| | 0.787 | 10 | not calc. |
| 2 2 $\bar{3}$ | | + 7 | |
| 4 1 3 | | − 33 | |
| | 0.843 | 34 | 25 |
| 4 1 $\bar{3}$ | | + 8 | |
| 3 3 3 | | − 9 | |
| | 0.878 | 13 | 6 |
| 3 3 $\bar{3}$ | | + 9 | |
| 5 2 3 | | − 2 | |
| | 0.944 | 2 | 7 |
| 5 2 $\bar{3}$ | | < −1 | |
| 4 4 3 | | + 3 | |
| | 0.991 | 4 | < 6 |
| 4 4 $\bar{3}$ | | − 3 | |
| 7 1 3 | | + 1 | |
| | 1.035 | 1 | < 7 |
| 7 1 $\bar{3}$ | | − 1 | |
| 6 3 3 | | + 21 | |
| | 1.064 | 21 | 19 |
| 6 3 $\bar{3}$ | | − 1 | |
| 5 5 3 | | + 5 | |
| | 1.120 | 7 | (4) |
| 5 5 $\bar{3}$ | | − 5 | |
| 8 2 3 | | − 16 | |
| | 1.159 | 16 | 15 |
| 8 2 $\bar{3}$ | | − 1 | |
| 7 4 3 | | + 3 | |
| | 1.198 | 3 | (4) |
| 7 4 $\bar{3}$ | | − 1 | |
| 6 6 3 | | + 5 | |
| | 1.259 | 7 | 8 |
| 6 6 $\bar{3}$ | | − 5 | |
| 10 1 3 | | − 6 | |
| | 1.271 | 6 | (5) |
| 10 1 $\bar{3}$ | | + 1 | |
| 9 3 3 | | − 4 | |
| | 1.295 | 5 | (5) |
| 9 3 $\bar{3}$ | | + 3 | |

TABLE II (*continued*).

| $h\,k\,l$ | $2 \sin \vartheta$ | $F_{c.}$ | | $F_{o.}$ | $h\,k\,l$ | $2 \sin \vartheta$ | $F_{c.}$ | | $F_{o.}$ |
|---|---|---|---|---|---|---|---|---|---|
| 8 5 3 | 1.341 | − 8 | 10 | 10 | 10 4 3 | 1.438 | + 1 | 3 | (5) |
| 8 5 $\bar{3}$ | | + 5 | | | 10 4 $\bar{3}$ | | + 3 | | |
| 11 2 3 | 1.407 | − 2 | 9 | 9 | 9 6 3 | 1.489 | + 3 | 7 | (5) |
| 11 2 $\bar{3}$ | | + 9 | | | 9 6 $\bar{3}$ | | − 6 | | |
| 7 7 3 | | < −1 | | | | | | | |
| 7 7 $\bar{3}$ | | < +1 | | | | | | | |

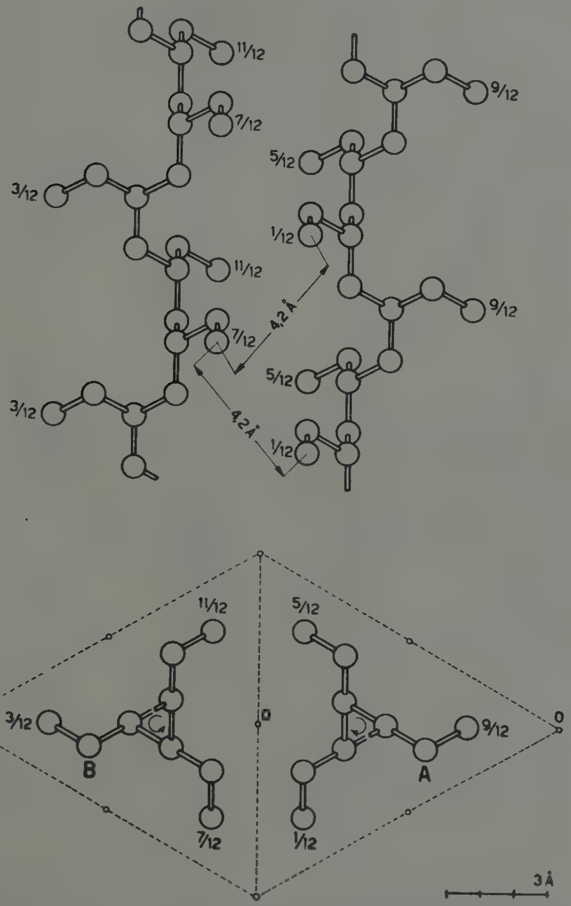

Fig. 12. – Projection on (0 0 1) and on a plane parallel to the *c* axis of two facing enantiomorphous macromolecules.

propylene, for which it is impossible to get a good filling of space in this way (Fig. 13).

It is worth noticing that 1,2 isotactic polybutadiene shows a structure closely analogous to that of poly-alpha-butene, differing only for the orientation of the lateral group and for small differences in the length of the *a* axis [10]. A similar structure is shown by polyvinylmethylether, whose X-ray diagram is closely similar to that of poly-alpha-butene. May be that in this case the molecules are somewhat more closely assembled since the

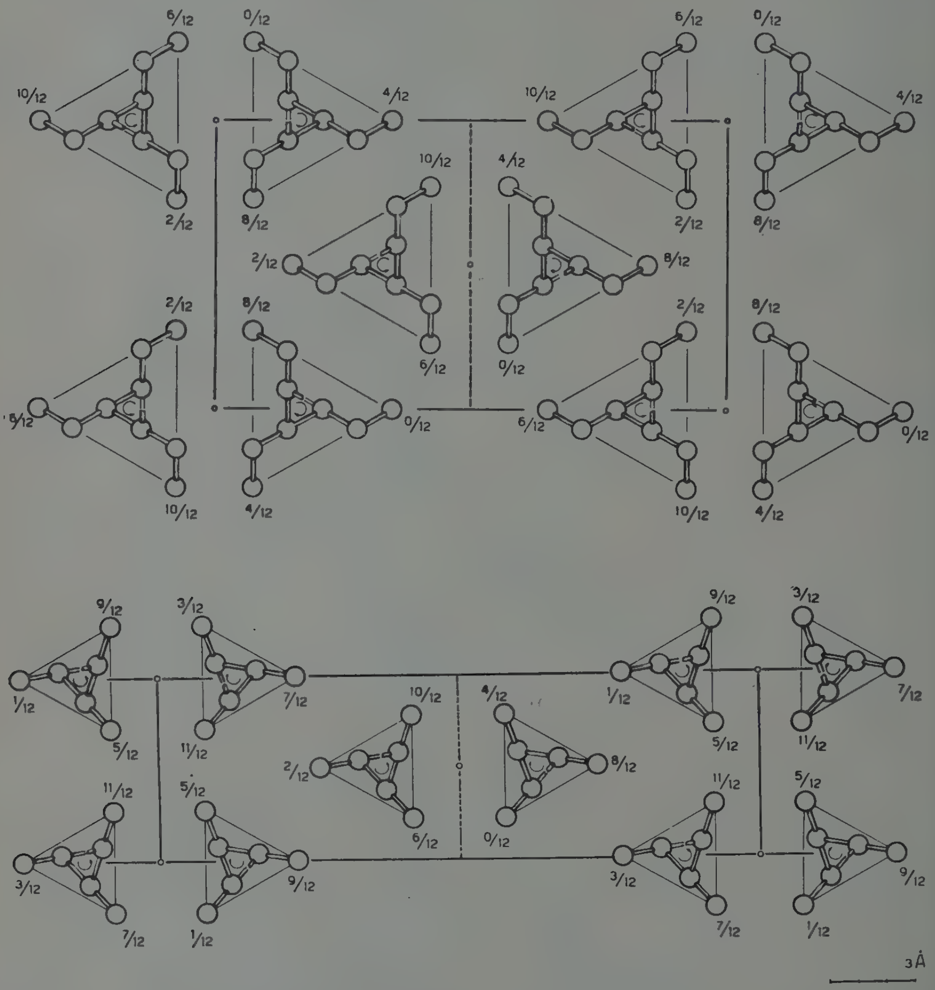

Fig. 13. Comparison between the packing realized by poly-alpha-butene and polypropylene macromolecules in the crystals.

TABLE III. - *Comparison between calculated and observed structure factors of poly-alpha-butene according to the R3c space group.*
(For the meaning of $F_{c.}$ and $F_{o.}$ see Table II. $B = 8.2$ Å$^2$).

| *h k l* | $F_{c.}$ | $F_{o.}$ | *h k l* | $F_{c.}$ | $F_{o.}$ |
|---|---|---|---|---|---|
| 1 1 0 | 69 | 115 | 7 2 $\bar{1}$ | 5 | (4) |
| 3 0 0 | 94 | 131 | 8 1 1 | 53 | 47 |
| 2 2 0 | 106 | 159 | 6 4 $\bar{1}$ | 19 | (4) |
| 4 1 0 | 38 | 17 | 7 3 1 | 6 | (4) |
| 3 3 0 | 4 | (2) | 6 5 1 | 37 | 35 |
| 6 0 0 | 34 | 51 | 9 1 $\bar{1}$ | | |
| 5 2 0 | 29 | 29 | 8 3 $\bar{1}$ | 11 | (5) |
| 4 4 0 | 1 | (3) | 9 2 1 | 1 | (5) |
| 7 1 0 | 44 | 38 | 7 5 $\bar{1}$ | 3 | (5) |
| 6 3 0 | 4 | (3) | 8 4 1 | 26 | 24 |
| 5 5 0 | 21 | 21 | 10 2 $\bar{1}$ | 6 | (5) |
| 9 0 0 | 9 | (3) | 7 6 1 | 5 | (5) |
| 8 2 0 | 7 | (3) | 11 1 1 | 27 | 29 |
| 7 4 0 | 25 | 25 | 9 4 $\bar{1}$ | | |
| 6 6 0 | 15 | 20 | 10 3 1 | 13 | (5) |
| 10 1 0 | 6 | (4) | 8 6 $\bar{1}$ | 8 | (6) |
| 9 3 0 | 24 | 26 | 9 5 1 | 4 | (6) |
| 8 5 0 | 14 | 18 | 12 1 $\bar{1}$ | 18 | < 11 |
| 12 0 0 | 10 | (4) | 11 3 $\bar{1}$ | 5 | < 7 |
| 11 2 0 | 38 | 35 | 8 7 1 | 4 | (6) |
| 7 7 0 | | | 12 2 1 | 4 | (6) |
| 10 4 0 | 16 | 22 | 10 5 $\bar{1}$ | 12 | 14 |
| 9 6 0 | 7 | (4) | 11 4 1 | 4 | (6) |
| 13 1 0 | 9 | < 8 | 9 7 $\bar{1}$ | 2 | (6) |
| 12 3 0 | 5 | < 5 | 10 6 1 | 16 | 19 |
| 8 8 0 | 3 | (4) | 13 2 $\bar{1}$ | | |
| 11 5 0 | 12 | 13 | 12 4 $\bar{1}$ | 2 | (6) |
| 10 7 0 | 10 | 8 | 14 1 1 | 2 | (6) |
| 15 0 0 | 3 | (4) | 13 3 1 | 5 | (6) |
| 14 2 0 | 3 | (4) | 9 8 1 | | |
| 13 4 0 | 2 | (4) | 11 6 $\bar{1}$ | 5 | (6) |
| 9 9 0 | 7 | (4) | 12 5 1 | 2 | (6) |
| 2 1 1 | 155 | 219 | 1 0 $\bar{2}$ | 62 | not calc. |
| 3 1 $\bar{1}$ | 65 | 50 | 2 0 2 | 26 | 13 |
| 3 2 1 | 34 | 28 | 2 1 $\bar{2}$ | 35 | 32 |
| 4 2 $\bar{1}$ | 28 | 19 | 3 1 2 | 18 | 15 |
| 5 1 1 | 99 | 88 | 4 0 $\bar{2}$ | 16 | 10 |
| 4 3 1 | 10 | (3) | 3 2 $\bar{2}$ | 12 | 17 |
| 6 1 $\bar{1}$ | 8 | (4) | 5 0 2 | 2 | (3) |
| 5 3 $\bar{1}$ | 7 | (4) | 4 2 2 | 22 | 21 |
| 6 2 1 | 76 | 48 | 5 1 $\bar{2}$ | 13 | 19 |
| 5 4 1 | 7 | (4) | 4 3 $\bar{2}$ | 21 | (3) |

TABLE III (*continued*).

| $h\,k\,l$ | $F_c$ | $F_o$ |
|---|---|---|
| $6\ 1\ 2$ | 35 | 28 |
| $7\ 0\ \bar{2}$ | 20 | 19 |
| $5\ 3\ 2$ | | |
| $6\ 2\ \bar{2}$ | 12 | 15 |
| $5\ 4\ \bar{2}$ | 9 | (4) |
| $8\ 0\ 2$ | 24 | 28 |
| $7\ 2\ 2$ | 9 | (4) |
| $8\ 1\ \bar{2}$ | 12 | $< 9$ |
| $6\ 4\ 2$ | 6 | (4) |
| $7\ 3\ \bar{2}$ | 7 | (4) |
| $6\ 5\ \bar{2}$ | 18 | 18 |
| $9\ 1\ 2$ | | |
| $8\ 3\ 2$ | 6 | (5) |
| $10\ 0\ \bar{2}$ | 6 | (5) |
| $9\ 2\ \bar{2}$ | 1 | (5) |
| $7\ 5\ 2$ | 15 | $< 10$ |
| $8\ 4\ \bar{2}$ | | |
| $11\ 0\ 2$ | 3 | (5) |
| $10\ 2\ 2$ | 6 | $< 10$ |
| $7\ 6\ \bar{2}$ | 9 | $< 10$ |
| $9\ 4\ 2$ | 11 | 11 |
| $11\ 1\ \bar{2}$ | | |
| $10\ 3\ \bar{2}$ | $< 1$ | (5) |
| $8\ 6\ 2$ | 10 | 12 |
| $9\ 5\ \bar{2}$ | 4 | (5) |
| $12\ 1\ 2$ | 4 | (6) |
| $1\ 1\ 3$ | 71 | not calc. |
| $1\ 1\ \bar{3}$ | | |
| $2\ 2\ 3$ | 11 | not calc. |
| $2\ 2\ \bar{3}$ | | |
| $4\ 1\ 3$ | 39 | 31 |
| $4\ 1\ \bar{3}$ | | |
| $3\ 3\ 3$ | 22 | 8 |
| $3\ 3\ \bar{3}$ | | |
| $5\ 2\ 3$ | 6 | 9 |
| $5\ 2\ \bar{3}$ | | |
| $4\ 4\ 3$ | 17 | $< 8$ |
| $4\ 4\ \bar{3}$ | | |
| $7\ 1\ 3$ | 7 | $< 9$ |
| $7\ 1\ \bar{3}$ | | |
| $6\ 3\ 3$ | 24 | 24 |
| $6\ 3\ \bar{3}$ | | |
| $5\ 5\ 3$ | 8 | (4) |
| $5\ 5\ \bar{3}$ | | |
| $8\ 2\ 3$ | 17 | 19 |
| $8\ 2\ \bar{3}$ | | |
| $7\ 4\ 3$ | 15 | (5) |
| $7\ 4\ \bar{3}$ | | |
| $6\ 6\ 3$ | 14 | 10 |
| $6\ 6\ \bar{3}$ | | |
| $10\ 1\ 3$ | 11 | (5) |
| $10\ 1\ \bar{3}$ | | |
| $9\ 3\ 3$ | 6 | (5) |
| $9\ 3\ \bar{3}$ | | |
| $8\ 5\ 3$ | 19 | 13 |
| $8\ 5\ \bar{3}$ | | |
| $11\ 2\ 3$ | 11 | $< 11$ |
| $11\ 2\ \bar{3}$ | | |
| $7\ 7\ 3$ | | |
| $7\ 7\ \bar{3}$ | | |
| $10\ 4\ 3$ | 4 | (5) |
| $10\ 4\ \bar{3}$ | | |
| $9\ 6\ 3$ | 10 | (5) |
| $9\ 6\ \bar{3}$ | | |

allowed Van der Waals contacts between $CH_3$ and O are expected to be lower, with regard to the correspondent contacts between methyl and methylene groups.

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SUPPLEMENTO AL VOLUME XV, SERIE X
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# Crystal Structure of Isotactic Polystyrene.

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(ricevuto il 26 Giugno 1959)

The investigation by X-rays [1] and by electron beams [2] of the styrene polymers, obtained with stereospecific catalysts [3], was made at the Institute of Industrial Chemistry of the Milan Polytechnic, as part of our research work on the crystal structure of isotactic polymers. The results issued from a preliminary examination have been outlined in a preceding Letter to the Editor of *Makromolekulare Chemie* [4].

## 1. – Experimental.

The isotactic polymers of styrene display at X-ray examination a crystallinity of $(40 \div 45)\%$ [5]. They show a very high melting point (up to 240 °C) [6], and, therefore, substantially differ from styrene polymers precedently known, which are amorphous and possess a softening point (II order transition) which is not higher than 90 °C.

The crystallization of high molecular weight isotactic polystyrene occurs very slowly; quenching the polymer from the melted state down to room temperature it does not crystallize. The so treated amorphous isotactic polymers of styrene become soluble in ketonic solvents *i.e.* methylethylketone in which the atactic polymers with the same molecular weight are soluble and, heated, they soften at 90 °C. Above this temperature, they can crystallize and become insoluble in the above mentioned solvents. For example, some characteristic kinetic curves of crystallization, obtained by a special apparatus that we have designed [7], are reported in Fig. 1. The fractions in weight of the crystallized polymer are plotted therein against time, for various temperatures [8]. The crystallization rate is strongly dependent on the molecular weight, and it reaches its highest degree at temperatures of about 180 °C.

Oriented crystalline fibers of polystyrene, allowing to perform a roentgenographic examination of the structure of the polymer, could be obtained in the following way.

The polymer is extruded at 250 °C, in order to obtain a small cylinder.

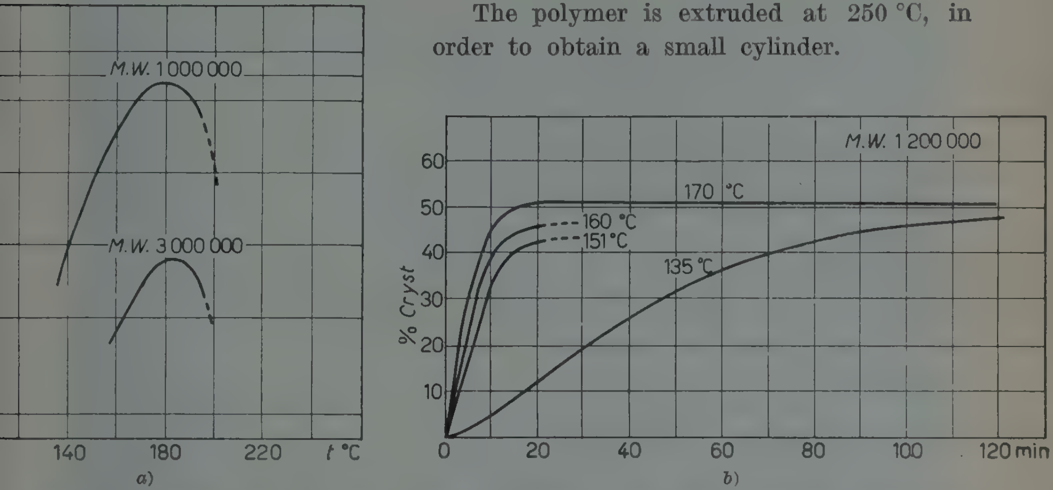

Fig. 1. – Crystallization kinetics curves of different samples of isotactic polystyrene (the molecular weight here reported is that measured before performing the experiences).

When quickly cooled down to room temperature, it results amorphous owing to the low crystallization rate. The extruded filament is then stretched at a temperature (about 100 °C) slightly higher than the softening temperature of the amorphous polymer and allowed to crystallize under tension at 150 °C during (2 ÷ 3) hours.

The fiber obtained by this method gives an X-ray spectrum, very rich of well oriented reflections (Fig. 2). The spectrum may be readily interpreted by reciprocal lattice methods on the basis of a rhombohedral unit cell (only reflections with $-h+k+l=3n$ are present) whose identity periods referred to hexagonal axes are: $a=b=(21.9 \pm 0.1)$ Å and $c=(6.65 \pm 0.05)$ Å ($c$ is the axis of the polymeric chain and coincides with the stretching direction).

Should one assume that the number of monomeric units contained in the unit cell is 18, the calculated density ($d_{\text{calc.}} = 1.126$ g/cm³) is in accordance with the experimental datum ($d_{\text{exp.}} = 1.08$ g/cm³). From the further systematical absence of reflections $(h0l)$ with $l=2n+1$, the choice of the space group is restricted to the $R\bar{3}c$ space group or to its subgroup $R3c$.

The measurement of the reflection intensities was carried out by the multiple film method, and it was possible, in a quantitative way, only for the zero and the 1st layer lines of the fiber photograph.

For the 2nd and 3rd layer lines, which show much enlarged spots with intensities which are thus rather difficult to be evaluated quantitatively, we shall outline only the qualitative course of the diffracted intensities (see below).

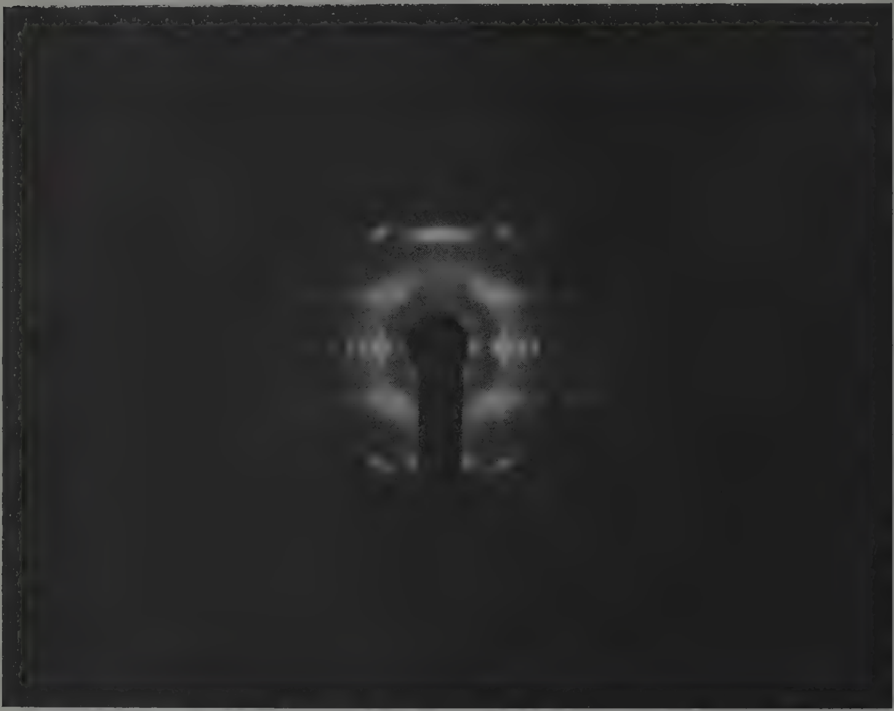

Fig. 2. – Fiber photograph of isotactic polystyrene.

## 2. – Considerations on the structure.

The monomeric units, according to reasons analogous to those illustrated for poly-alpha-butene [9], must necessarily follow one another along a three-fold screw axis. It is possible, therefore, to construct a model of the chain even when only the identity period along the chain axis is known (6.65 Å), keeping into account the principles summarized in a previous work of ours [10].

Such a model is shown in Fig. 3. In Fig. 4, a small portion of the chain itself is sketched. If one wishes that the atoms of the chain obey the principle of staggered bonds, the $C_1\widehat{C_2}C_{1'}$ and $C_2\widehat{C_1}C_{2''}$ angles must be equal to 116°. The most probable position of the plane on which the benzene ring lies, is that in which the plane bisects the $C_1\widehat{C_2}C_{1'}$ angle [11].

In such a way, unsuitable Van der Waals contacts between carbon atoms belonging to the same chain, are minimized; in particular $C_4$ and $C_5$ have respectively the same distance from $C_{1'}$ and $C_1$.

In a first instance, the tetrahedral value (109° 28′) has been assumed for the $\widehat{C_{1'}C_2}C_3$ and $\widehat{C_1C_2}C_3$ angles analogously to what we found for poly-alphabutene. Successively, these angles have been slightly modified in order to obtain the best accordance between observed and calculated structure factors. Such values, reported in Fig. 4, are respectively 108° ($\widehat{C_1C_2}C_3$) and 111° ($\widehat{C_{1'}C_2}C_3$).

The determination of the co-ordinates of the independent structural unit, was performed by us, keeping into account the particular intensity of some equatorial reflections by means of structure factor graphs [12] and by assuming that the Van der Waals contacts between the atoms of neighbouring macromolecules, should be in reasonable accordance with those given in the literature for low molecular weight compounds.

The determination of the probable orientation of the macromolecules around the threefold screw axes of the crystal lattice was facilitated when the (220)

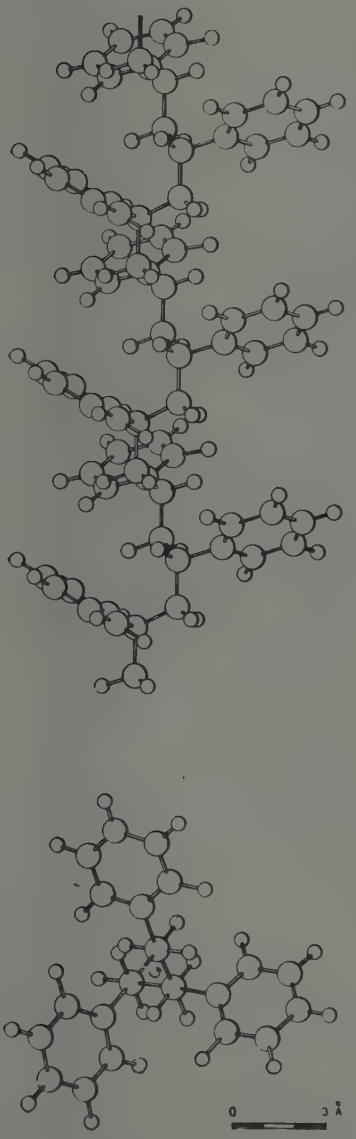

Fig. 3. – Conformation of the isotactic polystyrene macromolecule in the crystalline state (side and end views).

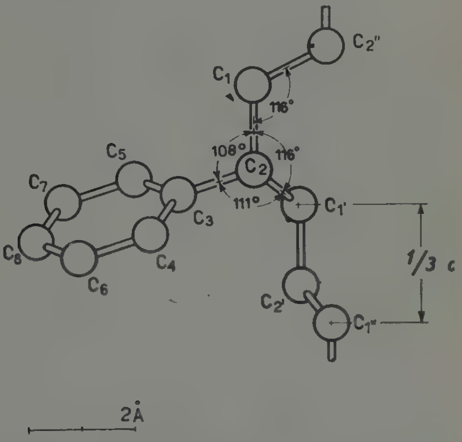

Fig. 4. – Conformation of the independent structural unit of isotactic polystyrene. ($C{-}C = 1.54$ Å, $(C{-}C)_{bz} = 1.40$ Å).

and (6 6 0) reflections, both particularly intense, were considered. Their structure factors do not vary in respect to the choice of the space group (*R3c* or *R$\bar{3}$c*) [13] which choice, in the first phase of researches, did not seem possible to be done.

The structure factor graphs of the (2 2 0) and (6 6 0) reflections are shown in Fig. 5 and 6, together with the position which the independent structural unit is approximately expected to assume, in order to get these reflections to have high intensity. The effective co-ordinates of the independent structural unit have been then more rigorously determined, considering the Van der Waals contacts occurring, by rotation of the macromolecule in a narrow range around its threefold screw axis. According to what required by the *R3c* space group, we analysed first the contacts between macromolecules facing each other through glide planes with translation along *c*. The attention was retained first on the *R3c* space group since it is a subgroup of the other possible space group, *R$\bar{3}$c*. In Fig. 7 is shown the position of the structural

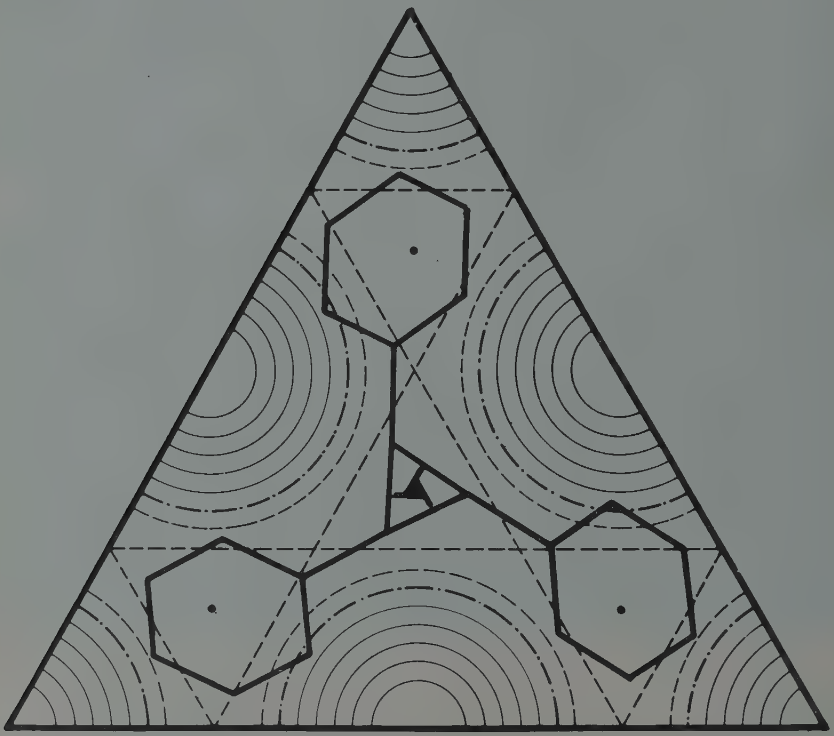

Fig. 5. – (2 2 0) structure factor graph, showing the position assumed by the macromolecule (contours are drawn at regular intervals: ——— positive lines; –·–·–·– zero lines; – – – – negative lines).

unit ($A$), which minimizes the Van der Waals contacts between carbon atoms of adjacent macromolecules. By rotating the independent unit by 2° either clockwise or anticlockwise, the Van der Waals contacts become already remarkably worse (see Table I) and the distances between C atoms of neighbouring chains result lower than the values recorded for other solved structures ((3.4 ÷ 3.7) Å). Because of the frequent occurrence in polymers of phenomena of statistical vicariance [14], the possibility that the space group were $R\bar{3}c$ was also taken into consideration. In fact, the $R\bar{3}c$ space group leads necessarily to the possible statistical presence around the same threefold screw axis of isomorphous anticlined macromolecules, by the addition of a center of symmetry to the symmetry elements of the $R3c$ space group.

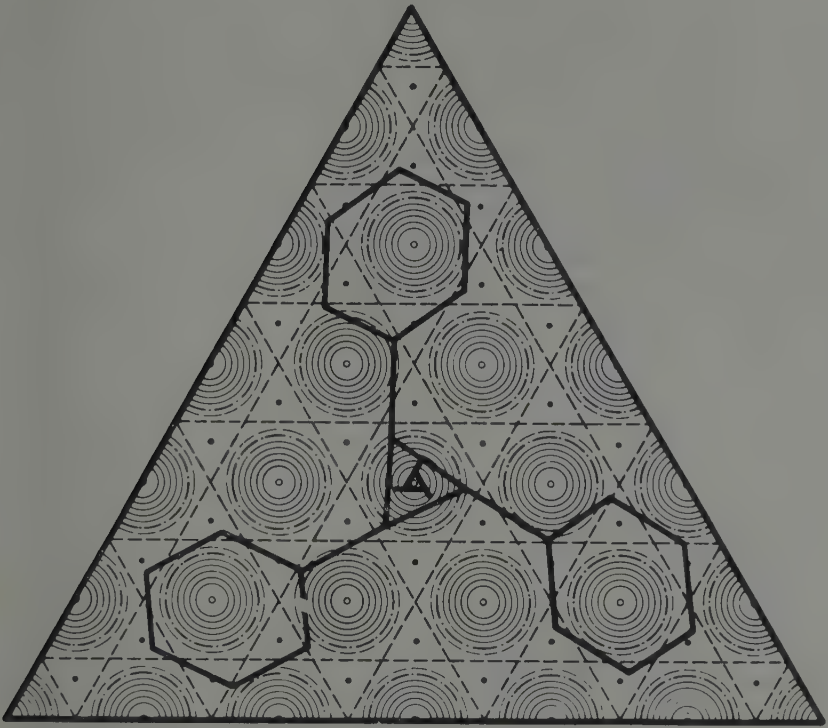

Fig. 6. – (660) structure factor graph.

A choice is not possible on the basis of Van der Waals contacts between neighbouring molecules. In fact, after choosing, in a suitable way, the origin along the $z$ axis, as indicated in Fig. 7, the macromolecule, isomorphous of $A$ and anticlined to it (dashed in Fig. 7), that may vicariate $A$ around the same threefold screw axis, shows Van der Waals distances in respect of C and B, which are even higher than 3.5 Å.

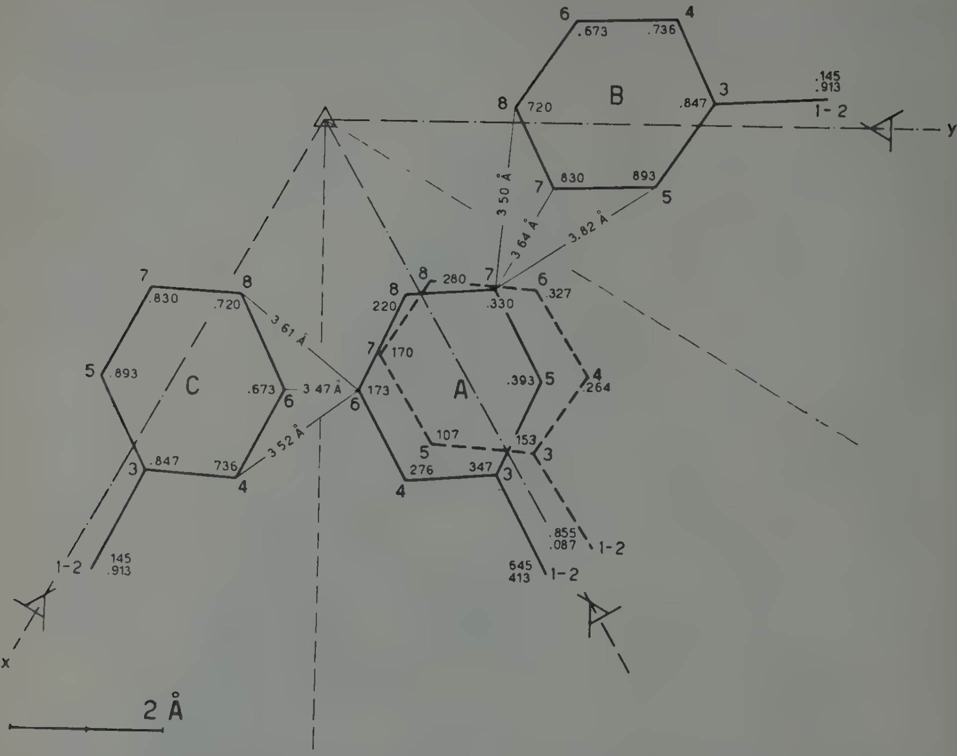

Fig. 7. - Actual position of the independent structural unit ($A$) in the unit cell. The anticlined macromolecule in respect of $A$ and possible statistical vicariant of $A$ itself, is dashed.

TABLE I. *Values of the Van der Waals contact distances among atoms of neighbouring macromolecules (only the most significant values are reported).*
I. Values calculated when the position assumed by the macromolecule is that of Fig. 7.
II. III. Values obtained after rotating the macromolecule around its threefold screw axis by 2°, anticlockwise and clockwise respectively.

| Atoms of isoclined molecules (Full drawn in Fig. 7) | | II Å | I Å | III Å | Atoms of anticlined molecules | | I Å |
|---|---|---|---|---|---|---|---|
| $C_{7A}$ | $C_{7B}$ | 3.76 | 3.64 | 3.57 | $C_{6A}$ | $C_{7B}$ | 3.56 |
| $C_{7A}$ | $C_{5B}$ | 3.95 | 3.82 | 3.72 | $C_{6A}$ | $C_{8B}$ | 3.52 |
| $C_{7A}$ | $C_{8B}$ | 3.68 | 3.50 | 3.36 | $C_{6A}$ | $C_{5B}$ | 3.54 |
| $C_{6A}$ | $C_{6C}$ | 3.42 | 3.47 | 3.54 | $C_{8A}$ | $C_{7B}$ | 3.59 |
| $C_{6A}$ | $C_{8C}$ | 3.54 | 3.61 | 3.75 | $C_{8A}$ | $C_{8B}$ | 3.85 |
| $C_{6A}$ | $C_{4C}$ | 3.44 | 3.52 | 3.62 | $C_{4A}$ | $C_{5B}$ | 3.60 |
| | | | | | $C_{4A}$ | $C_{7B}$ | 3.81 |

## 3. – Calculation of the structure factors.

We found it advisable to make the calculations of the structure factors for both space groups, owing to the above seen impossibility of choosing between them on the basis of possible unsuitable Van der Waals contacts. The calculation of the structure factors comprising also the contribution of hydrogen atoms, was performed for the previously suggested model and for some different models in which the independent structural unit was allowed to slightly rotate around its threefold screw axis or in which the benzene ring was allowed to slightly rotate around the $C_2$—$C_3$ bond (Fig. 7 and Fig. 4).

The best results were obtained just for the model sketched in Fig. 4 which was most convincing from a stereochemical viewpoint, and by the co-ordinates plotted in Table II.

Table II. – *Coordinates of the independent structural unit.*
(The index of the hydrogen atoms refers to the carbon atoms they are linked to, the carbon atoms are marked as in Fig. 4).

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| $C_1$ | 0.308 | 0.290 | 0.645 |
| $C_2$ | 0.308 | 0.290 | 0.413 |
| $C_3$ | 0.240 | 0.226 | 0.347 |
| $C_4$ | 0.245 | 0.173 | 0.236 |
| $C_5$ | 0.176 | 0.219 | 0.393 |
| $C_6$ | 0.184 | 0.114 | 0.173 |
| $C_7$ | 0.114 | 0.160 | 0.330 |
| $C_8$ | 0.118 | 0.108 | 0.220 |
| $H_1$ | 0.304 | 0.241 | 0.700 |
| $H_1'$ | 0.263 | 0.294 | 0.700 |
| $H_2$ | 0.354 | 0.287 | 0.358 |
| $H_4$ | 0.296 | 0.178 | 0.200 |
| $H_5$ | 0.174 | 0.261 | 0.479 |
| $H_6$ | 0.187 | 0.074 | 0.086 |
| $H_7$ | 0.062 | 0.154 | 0.367 |
| $H_8$ | 0.071 | 0.063 | 0.170 |

The accordance is good as well, either by assuming that the space group is $R\bar{3}c$, or that it is $R3c$ (Tables III and IV).

It must be noticed that, owing to the difficulty of the visual measurement of intensities, the values of $F_o$ may be affected by absolute errors fairly appreciable. Fortunately there is evidence to believe that such errors are monotonous functions of the diffraction angle and thus, in making the accordance, are compensated through the thermal factor applied to the calculated structure

TABLE III. – *Comparison between the observed and calculated structure factors for the $R\bar{3}c$ space group.* $B = 11$ Å$^2$.

The $F_{o.}$ values correspond to the square root of the total intensity diffracted by the general ($hkl$) lattice plane, after effecting the corrections for the usual angular factors. In order to take the different multiplicity of the reflections into account, all the calculated structure factors except the ($h00$) and ($hh0$) ones, were multiplied by $\sqrt{2}$. (Cu, K α).

| *h k l* | 2 sin ϑ | $F_{c.}$ | $F_{o.}$ |
|---|---|---|---|
| 1 1 0 | 0.141 | −36 | 33 |
| 3 0 0 | 0.245 | +53 | 67 |
| 2 2 0 | 0.282 | −177 | 182 |
| 4 1 0 | 0.373 | −40 | 43 |
| 3 3 0 | 0.425 | +53 | 59 |
| 6 0 0 | 0.487 | +13 | — |
| 5 2 0 | 0.508 | −34 | 33 |
| 4 4 0 | 0.564 | +22 | 21 |
| 7 1 0 | 0.614 | −1 | — |
| 6 3 0 | 0.645 | +40 | 53 |
| 5 5 0 | 0.704 | −30 | 33 |
| 9 0 0 | 0.732 | +7 | — |
| 8 2 0 | 0.746 | +28 | 34 |
| 7 4 0 | 0.784 | −13 | — |
| 6 6 0 | 0.845 | −53 | 66 |
| 10 1 0 | 0.856 | +7 | — |
| 9 3 0 | 0.880 | −6 | — |
| 8 5 0 | 0.923 | +1 | — |
| 12 0 0 | 0.976 | −1 | — |
| 11 2 0 | 0.986 | +10 | 17 |
| 7 7 0 | | + | |
| 10 4 0 | 1.016 | +13 | 17 |
| 9 6 0 | 1.062 | −4 | — |
| 13 1 0 | 1.099 | −3 | — |
| 12 3 0 | 1.118 | −12 | 15 |
| 8 8 0 | 1.127 | +3 | — |
| 11 5 0 | 1.153 | +2 | — |
| 10 7 0 | 1.204 | +4 | — |
| 15 0 0 | 1.221 | −14 | 17 |
| 14 2 0 | 1.227 | −3 | — |
| 13 4 0 | 1.252 | +12 | 12 |
| 9 9 0 | 1.267 | −1 | — |
| 12 6 0 | 1.290 | −4 | — |
| 16 1 0 | 1.343 | +14 | 15 |
| 11 8 0 | | − | |
| 15 3 0 | 1.358 | −8 | — |
| 14 5 0 | 1.387 | −3 | — |
| 10 10 0 | 1.408 | +3 | — |
| 2 1 1 | 0.318 | +224 | 249 |
| 3 1 $\bar{1}$ | 0.374 | −135 | 128 |
| 3 2 1 | 0.423 | +56 | 67 |
| 4 2 $\bar{1}$ | 0.489 | −89 | 71 |
| 5 1 1 | 0.508 | −50 | 39 |
| 4 3 1 | 0.546 | −4 | — |
| 6 1 $\bar{1}$ | 0.581 | +16 | — |
| 5 3 $\bar{1}$ | 0.614 | −84 | 83 |
| 6 2 1 | 0.630 | +4 | — |
| 5 4 1 | 0.675 | +33 | 40 |
| 7 2 $\bar{1}$ | 0.704 | +27 | 34 |
| 8 1 1 | 0.731 | −31 | — |
| 6 4 $\bar{1}$ | 0.745 | −43 | 43 |
| 7 3 1 | 0.759 | −59 | 75 |
| 6 5 1 | 0.809 | +34 | 45 |
| 9 1 $\bar{1}$ | | + | |
| 8 3 $\bar{1}$ | 0.833 | +1 | — |
| 9 2 1 | 0.857 | −4 | — |
| 7 5 $\bar{1}$ | 0.879 | −3 | — |
| 8 4 1 | 0.891 | +9 | — |
| 10 2 $\bar{1}$ | 0.917 | −8 | — |
| 7 6 1 | 0.944 | −10 | — |
| 11 1 1 | 0.965 | +6 | — |
| 9 4 $\bar{1}$ | | + | |
| 10 3 1 | 0.985 | −3 | — |
| 8 6 $\bar{1}$ | 1.018 | −10 | — |
| 9 5 1 | 1.024 | +16 | 27 |
| 12 1 $\bar{1}$ | 1.042 | +15 | |
| 11 3 $\bar{1}$ | 1.062 | −1 | — |
| 8 7 1 | 1.081 | −15 | — |
| 12 2 1 | 1.089 | +23 | 23 |
| 10 5 $\bar{1}$ | 1.098 | −7 | — |
| 11 4 1 | 1.117 | +5 | — |
| 9 7 $\bar{1}$ | 1.154 | +9 | — |

| *h k l* | 2 sin ϑ | Int.$_{c.}$ | Int.$_{o.}$ |
|---|---|---|---|
| 1 0 $\bar{2}$ | 0.471 | not calc. | vs |
| 2 0 2 | 0.493 | 2118 | m |
| 2 1 $\bar{2}$ | 0.512 | 795 | mw |
| 3 1 2 | 0.548 | 7862 | ms |
| 4 0 $\bar{2}$ | 0.566 | 1453 | m |
| 3 2 $\bar{2}$ | 0.583 | 83 | — |

TABLE III (*continued*).

| *h k l* | 2 sin ϑ | Int.c. | Int.o. | *h k l* | 2 sin ϑ | Intc. | Into. |
|---|---|---|---|---|---|---|---|
| 5 0 2 | 0.618 | 470 | mw | 8 4 $\bar{2}$ | 0.976 | 4 | — |
| 4 2 2 | 0.634 | 174 | w | 11 0 2 | 1.007 | 10 | — |
| 5 1 $\bar{2}$ | 0.648 | 61 | — | 10 2 2 | 1.017 | 16 | — |
| 4 3 $\bar{2}$ | 0.678 | 91 | w | 7 6 $\bar{2}$ | 1.026 | 7 | — |
| 6 1 2 | 0.694 | 65 | — | 9 4 2 } | 1.045 | 15 | vvw |
| 7 0 $\bar{2}$ } | 0.733 | 437 | mw | 11 1 $\bar{2}$ } | | | |
| 5 3 2 } | | | | 10 3 $\bar{2}$ | 1.064 | — | — |
| 6 2 $\bar{2}$ | 0.747 | 10 | — | 8 6 2 | 1.091 | 1 | — |
| 5 4 $\bar{2}$ | 0.788 | 61 | — | | | | |
| 8 0 2 | 0.798 | 50 | — | 1 1 3 (*) | 0.711 | not calc. } | s |
| 7 2 2 | 0.810 | 173 } | w | 2 2 3 | 0.752 | 1956 } | |
| 8 1 $\bar{2}$ | 0.835 | 169 } | | 4 1 3 | 0.791 | 371 | w |
| 6 4 2 | 0.847 | 2 | — | 3 3 3 | 0.816 | 678 | mw |
| 7 3 $\bar{2}$ | 0.859 | 5 | — | 5 2 3 | 0.862 | 815 | m |
| 6 5 $\bar{2}$ } | 0.903 | 183 | w | 4 4 3 | 0.897 | 101 | — |
| 9 1 2 } | | | | 7 1 3 | 0.929 | 33 | — |
| 8 3 2 | 0.925 | 12 | — | 6 3 3 | 0.946 | 172 | vw |
| 10 0 $\bar{2}$ | 0.936 | 3 | — | 5 5 3 | 0.989 | 37 | — |
| 9 2 $\bar{2}$ | 0.945 | 38 } | vw | 8 2 3 | 1.021 | 2 | — |
| 7 5 2 | 0.967 | 26 } | | 7 4 3 | 1.049 | 11 | — |

(*) The calculated intensity of *h k* 3 reflections is the sum of the diffracted intensities of both (*h k* 3) and (*h k* $\bar{3}$) lattice planes.

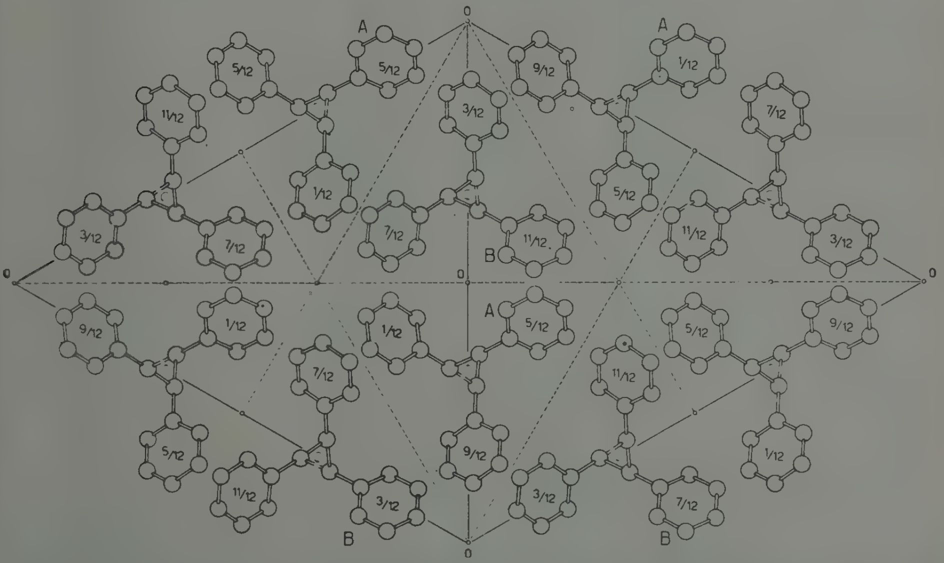

Fig. 8. – Projection on (0 0 1) of the structure of isotactic polystyrene for the *R*3*c* space group.

TABLE IV. - *Comparison between the observed and calculated structure factors for the R3c space group. For the meaning of* $F_{c.}$ *and* $F_{o.}$ see Table II. $B = 9.5$ Å$^2$.

| h k l | A | B | $F_{c.}$ | $F_{o.}$ |
|---|---|---|---|---|
| 1 1 0 | — 37 | — | 37 | 40 |
| 3 0 0 | + 54 | — 53 | 76 | 81 |
| 2 2 0 | —179 | — | 179 | 220 |
| 4 1 0 | — 41 | + 25 | 48 | 52 |
| 3 3 0 | + 55 | — | 55 | 71 |
| 6 0 0 | + 14 | — 11 | 18 | — |
| 5 2 0 | — 34 | + 3 | 34 | 40 |
| 4 4 0 | + 23 | — | 23 | 25 |
| 7 1 0 | — 1 | + 21 | 21 | — |
| 6 3 0 | + 42 | — 49 | 65 | 65 |
| 5 5 0 | — 32 | — | 32 | 39 |
| 9 0 0 | + 7 | — 4 | 8 | — |
| 8 2 0 | + 30 | — 1 | 30 | 41 |
| 7 4 0 | — 14 | — 16 | 21 | — |
| 6 6 0 | — 59 | — | 59 | 79 |
| 10 1 0 | + 8 | + 7 | 11 | — |
| 9 3 0 | — 7 | — 22 | 23 | — |
| 8 5 0 | + 1 | + 32 | 32 | — |
| 12 0 0 | — 2 | — 12 | 12 | — |
| 11 2 0 | + 4 | + 22 | 25 | 20 |
| 7 7 0 | + 11 | — | | |
| 10 4 0 | + 16 | + 12 | 20 | 20 |
| 9 6 0 | — 5 | + 4 | 6 | — |
| 13 1 0 | — 3 | + 9 | 10 | — |
| 12 3 0 | — 15 | — 15 | 21 | 18 |
| 8 8 0 | + 4 | — | 4 | — |
| 11 5 0 | + 3 | <+1 | 3 | — |
| 10 7 0 | + 5 | + 2 | 5 | — |
| 15 0 0 | — 18 | — 37 | 41 | 21 |
| 14 2 0 | — 4 | + 3 | 5 | — |
| 13 4 0 | + 15 | + 4 | 16 | 15 |
| 9 9 0 | — 1 | — | 1 | — |
| 12 6 0 | — 5 | — 3 | 6 | — |
| 16 1 0 | + 18 | + 7 | 19 | 18 |
| 11 8 0 | — 2 | <—1 | | |
| 15 3 0 | — 11 | — 1 | 11 | — |
| 14 5 0 | — 4 | + 3 | 5 | — |
| 10 10 0 | + 4 | — | 4 | — |
| 2 1 1 | +228 | —139 | 267 | 301 |
| 3 1 $\bar{1}$ | —137 | — 38 | 142 | 155 |
| 3 2 1 | + 57 | + 99 | 114 | 81 |
| 4 2 $\bar{1}$ | — 90 | — 37 | 97 | 86 |
| 5 1 1 | — 51 | — 43 | 67 | 47 |
| 4 3 1 | — 4 | + 34 | 34 | — |
| 6 1 $\bar{1}$ | + 16 | + 26 | 31 | — |
| 5 3 $\bar{1}$ | — 87 | + 33 | 93 | 100 |
| 6 2 1 | + 4 | + 5 | 6 | — |
| 5 4 1 | + 35 | — 39 | 52 | 48 |
| 7 2 $\bar{1}$ | + 28 | — 13 | 31 | 41 |
| 8 1 1 | — 32 | — 32 | 45 | — |
| 6 4 $\bar{1}$ | — 47 | — 10 | 48 | 52 |
| 7 3 1 | — 64 | + 30 | 71 | 91 |
| 6 5 1 | + 19 | + 37 | 55 | 54 |
| 9 1 $\bar{1}$ | + 33 | + 13 | | |
| 8 3 $\bar{1}$ | + 1 | + 7 | 7 | — |
| 9 2 1 | — 5 | + 4 | 6 | — |
| 7 5 $\bar{1}$ | — 4 | — 38 | 38 | — |
| 8 4 1 | + 11 | — 13 | 17 | — |
| 10 2 $\bar{1}$ | — 9 | + 10 | 13 | — |
| 7 6 1 | — 12 | + 5 | 13 | — |
| 11 1 1 | + 6 | — 7 | 23 | — |
| 9 4 $\bar{1}$ | + 3 | — 21 | | |
| 10 3 1 | — 4 | — 5 | 6 | — |
| 8 6 $\bar{1}$ | — 12 | + 1 | 12 | — |
| 9 5 1 | + 19 | + 7 | 20 | 33 |
| 12 1 $\bar{1}$ | + 19 | + 4 | 19 | |
| 11 3 $\bar{1}$ | — 1 | + 1 | 1 | — |
| 8 7 1 | — 18 | — 9 | 20 | — |
| 12 2 1 | + 27 | + 31 | 41 | 28 |
| 10 5 $\bar{1}$ | — 8 | — 13 | 15 | — |
| 11 4 1 | + 7 | + 5 | 9 | — |
| 9 7 $\bar{1}$ | + 12 | + 8 | 14 | — |

factors $F_{c.}$. The thermal factor applied to $F_{c.}$, determined by studying the behaviour of ln $F_{c.}/F_{o.}$ as a function of $(\sin\vartheta/\lambda)^2$, has then to be assumed as the product of two terms, say the true thermal factor and a function of the scattering angle, which does compensate eventual errors of evaluation of the intensities (*e.g.* owing to the enlargement of spots on increasing of the scattering angle; owing to the blackening of the film, etc.).

Using the data we disposed of, it did not seem possible to us to choose univocally between the two space groups. It cannot be excluded that, inside

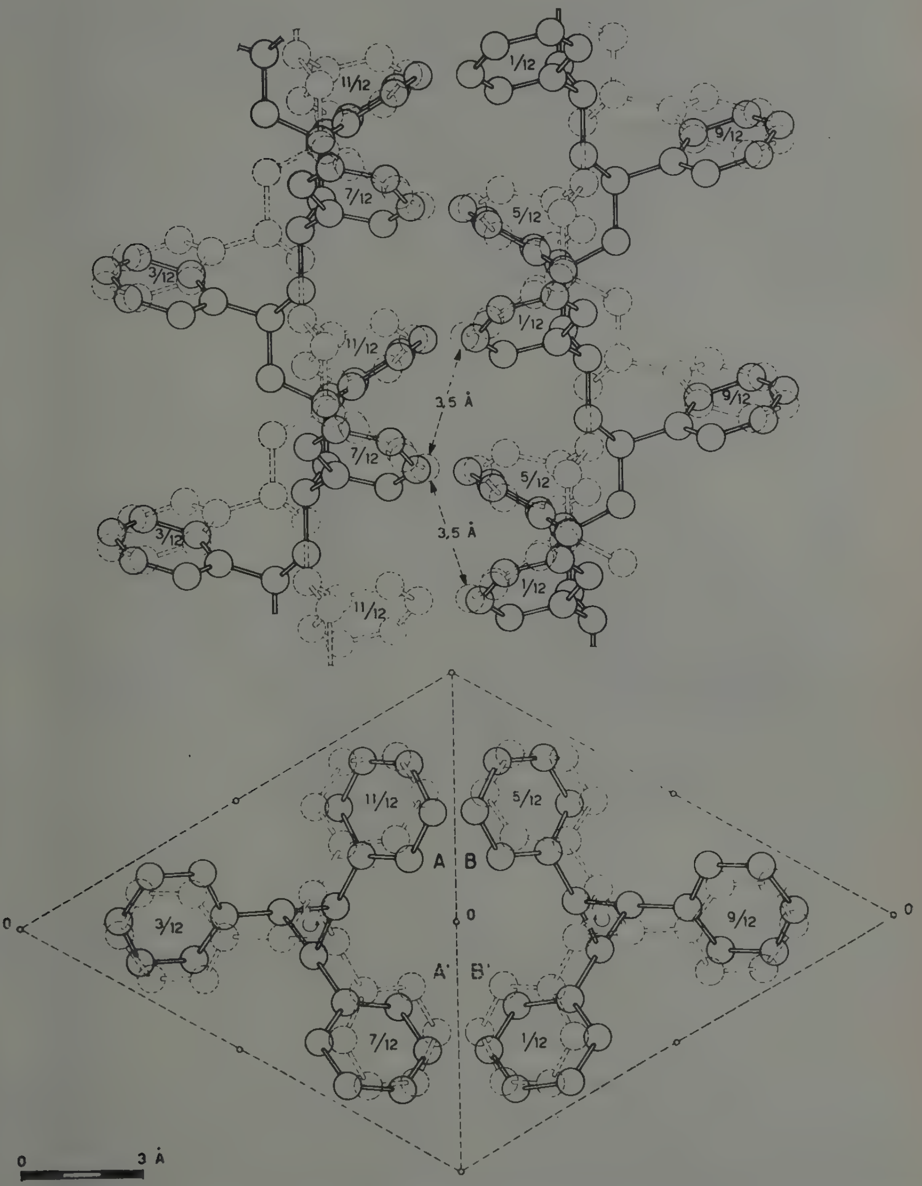

Fig. 9. – Model showing isosterism between anticlined isomorphous macromolecules.

any single crystal, as we supposed for polypropylene and poly-alpha-butene, the macromolecules are locally ranged according to the $R3c$ space group (Fig. 8) forming small blocks with a polar orientation. A larger crystal may be built up by an ensemble of such blocks, neighbouring one another in an anticlined way, in such a way as to keep unaltered the equatorial periodicity at the jointment planes. According to the magnitude of these blocks, the space group, as far as the diffraction effects are concerned, more approaches either the $R\bar{3}c$ or the $R3c$ space group. The assumption that each crystal is formed by small anticlined blocks, each formed by reciprocally isoclined macromolecules, seems to be reasonable when one thinks of the difficulty of separation of reciprocally anticlined macromolecules (which, from a kinetic point of view, should cause the formation of great polar aggregates to be somewhat difficult) and of the nature of the very similar Van der Waals contacts, which occur between enantiomorphous isoclined macromolecules and anticlined enantiomorphous ones (Fig. 9).

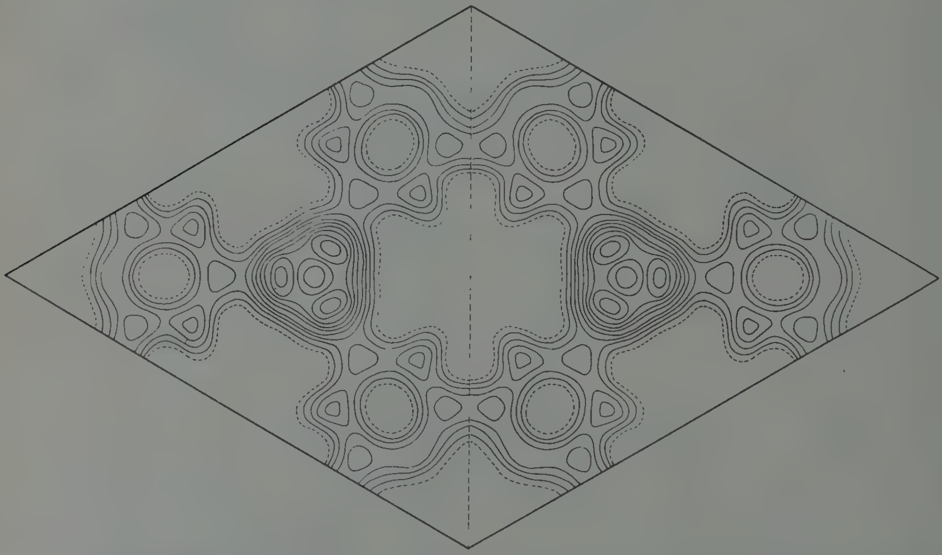

Fig. 10. – Projection on (001) of the electron density calculated according to the $R\bar{3}c$ space group (contours are drawn at 0.5 $e/\text{Å}^2$, the broken line is the 2 $e/\text{Å}^2$ level).

A similar kind of statistical vicariance was promoted by us in the case of the structure of natural rubber and, most probably, is in connection with the high value of the thermal factor.

With the signs obtained from the calculation of the structure factors according to the $R\bar{3}c$ space group of the equatorial reflections, a Fourier pro-

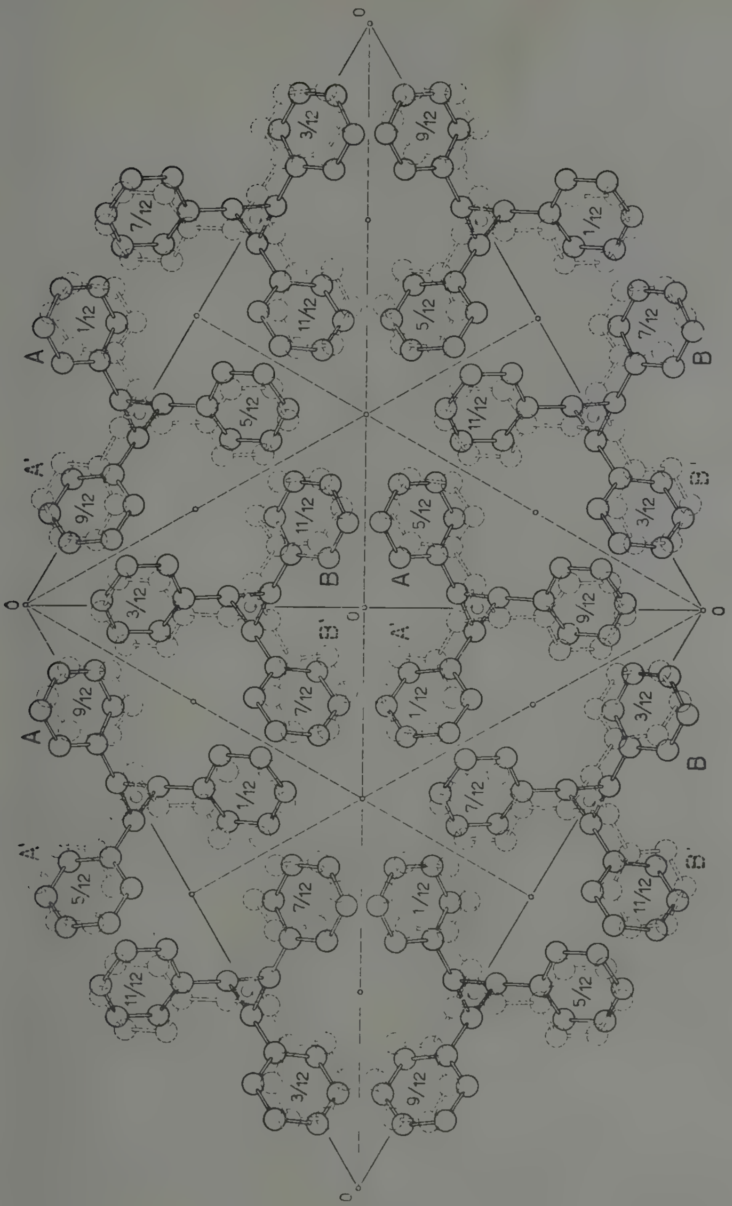

Fig. 11. - Projection on (001) of isotactic polystyrene structure according to the $R\bar{3}c$ space group. (For this space group, around the same threefold screw axis, isomorphous anticlined macromolecules may statistically vicariate).

jection of the electron density on the (001) plane has been calculated. As it may be realized from Fig. 10 either the positions of the monomeric units or their weights (see also Fig. 11) are in good accordance with the assumptions we have made.

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SUPPLEMENTO AL VOLUME XV, SERIE X
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# Crystal Structure of Poly-ortho-Fluorostyrene.

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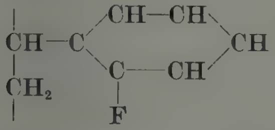
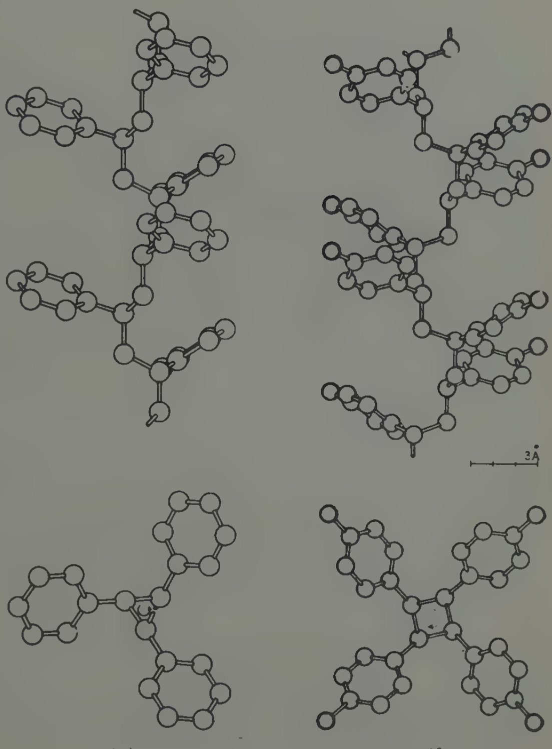
(ricevuto il 26 Giugno 1959)

Through processes of stereospecific catalysis, an isotactic crystalline [1] polymer of orthofluorostyrene [2]



was first synthesized at the Institute of Industrial Chemistry of the Milan Polytechnic.

We shall report, in the present work, the results of our roentgenographic researches carried on in view of establishing the mutual structure relations between this new polymer and the isotactic polystyrene previously studied by us [3].



1*a*)　　1*b*)

Fig. 1. – Conformation of the macromolecular chains of isotactic polystyrene (left) and of poly-para-fluorostyrene (right).

In a preceding work, it has been observed that, in the case of a p-substitution of a hydrogen atom of polystyrene by a fluorine atom, the form of the chain changed from that of threefold helix to that of a fourfold helix (Fig. 1) [4].

We shall see how the polymer we are considering in this paper has a structure strongly similar to that of isotactic polystyrene. Even an examination of the powder spectra of the two polymers, in fact, emphasizes the close analogy between them, at least as far as the form and dimensions of the unit cell are concerned (Fig. 2).

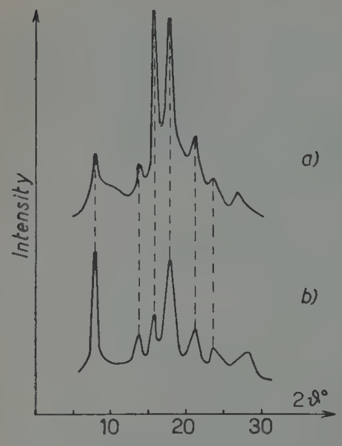


Fig. 2. – Comparison between the powder spectra (Cu, K$\alpha$) registered with Geiger counter of isotactic polystyrene (*a*) and poly-ortho-fluorostyrene (*b*).

## 1. – Experimental.

Samples able to supply oriented crystalline fibers were prepared by extruding a thin cylinder of polymer from the melt. Such a cylinder was submitted to unidirectional hot stretching and was annealed under tension at a temperature of about 150 °C. The specimen so obtained, examined by X-rays, gives fiber photographs with many well oriented reflections such as to allow a good structural investigation.

The indexing of the reflections by reciprocal lattice methods, was made on the basis, as for isotactic polystyrene, of a rhombohedral unit cell.

Referring the constants of this unit cell to hexagonal axes, we obtain:

$$a = b = (22.15 \pm 0.10)\ \text{Å} \qquad c = (6.63 \pm 0.05)\ \text{Å}\,.$$

The $c$ direction is coincident with the stretching axis and thus with the axis of the polymeric chain.

The density which may be calculated by assuming that 18 monomeric units are contained in the unit cell is 1.29 g/cm³.

The corresponding data for isotactic polystyrene are:

$$a = b = (21.9 \pm 0.1)\ \text{Å}\,, \quad c = (6.65 \pm 0.05)\ \text{Å}\,, \quad \varrho = 1.12\ \text{g/cm}^3\,.$$

In Table I are given the observed and calculated values of the Bragg distances for a cell having these unit translations.

TABLE I. – *Comparison between calculated and observed Bragg distances for poly-ortho-fluorostyrene.*

| *h k l* | $d_{c.}$ | $d_{o.}$ |
|---|---|---|
| 1 1 0 | 11.08 | 11.08 |
| 3 0 0 | 6.38 | 6.41 |
| 2 2 0 | 5.52 | 5.53 |
| 4 1 0 | 4.19 | 4.17 |
| 3 3 0 | 3.69 | 3.69 |
| 6 0 0 | 3.20 | 3.20 |
| 5 2 0 | 3.07 | 3.06 |
| 4 4 0 | 2.77 | 2.77 |
| 7 1 0 | 2.54 | 2.55 |
| 6 3 0 | 2.42 | 2.41 |
| 5 5 0 | 2.22 | 2.22 |
| 9 0 0 | 2.14 | 2.13 |
| 8 2 0 | 2.09 | 2.08 |
| 7 4 0 | 1.99 | 1.99 |
| 6 6 0 | 1.85 | 1.85 |
| 10 1 0 | 1.82 | — |
| 9 3 0 | 1.78 | — |
| 8 5 0 | 1.69 | 1.69 |
| 12 0 0 | 1.60 | — |
| 11 2 0<br>7 7 0 | 1.59 | 1.59 |
| 10 4 0 | 1.54 | — |
| 9 6 0 | 1.47 | — |
| 13 1 0 | 1.42 | — |
| 12 3 0 | 1.40 | — |
| 8 8 0 | 1.38 | — |
| 11 5 0 | 1.35 | — |
| 10 7 0 | 1.30 | — |
| 15 0 0 | 1.28 | 1.28 |
| 14 2 0 | 1.27 | — |
| 13 4 0 | 1.25 | — |
| 9 9 0 | 1.23 | — |
| 12 6 0 | 1.21 | — |
| 16 1 0<br>11 8 0 | 1.16 | 1.16 |
| 15 3 0 | 1.15 | — |
| 14 5 0 | 1.12 | — |
| 10 10 0 | 1.11 | — |
| 13 7 0 | 1.09 | — |
| 18 0 0 | 1.07 | 1.06 |
| 17 2 0 | 1.06 | — |
| 12 9 0 | 1.05 | — |
| 2 1 1 | 4.89 | 4.88 |
| 3 1 $\bar{1}$ | 4.15 | 4.11 |
| 3 2 1 | 3.67 | 3.66 |
| 4 2 $\bar{1}$ | 3.18 | 3.19 |
| 5 1 1 | 3.06 | 3.04 |
| 4 3 1 | 2.85 | 2.83 |
| 6 1 $\bar{1}$ | 2.68 | 2.68 |
| 5 3 $\bar{1}$ | 2.53 | 2.54 |
| 6 2 1 | 2.47 | — |
| 5 4 1 | 2.30 | 2.31 |
| 7 2 $\bar{1}$ | 2.21 | 2.21 |
| 8 1 1 | 2.13 | 2.16 |
| 6 4 $\bar{1}$ | 2.09 | — |
| 7 3 1 | 2.05 | 2.06 |
| 6 5 1<br>9 1 $\bar{1}$ | 1.92 | 1.93 |
| 8 3 $\bar{1}$ | 1.87 | 1.88 |
| 9 2 1 | 1.82 | — |
| 7 5 $\bar{1}$ | 1.77 | 1.78 |
| 8 4 1 | 1.75 | — |
| 10 2 $\bar{1}$ | 1.67 | — |
| 7 6 1 | 1.65 | — |
| 11 1 1<br>9 4 $\bar{1}$ | 1.61 | 1.63 |
| 10 3 1 | 1.58 | — |
| 8 6 $\bar{1}$ | 1.53 | — |
| 9 5 1 | 1.52 | — |
| 12 1 $\bar{1}$ | 1.49 | 1.49 |
| 11 3 $\bar{1}$ | 1.47 | — |
| 8 7 1 | 1.44 | — |
| 12 2 1 | 1.43 | — |
| 10 5 $\bar{1}$ | 1.42 | — |
| 11 4 1 | 1.40 | — |
| 1 0 $\bar{2}$ | 3.27 | not meas. |
| 2 0 2 | 3.12 | 3.13 |
| 2 1 $\bar{2}$ | 3.01 | — |
| 3 1 2 | 2.81 | 2.81 |
| 4 0 $\bar{2}$ | 2.72 | — |
| 3 2 $\bar{2}$ | 2.64 | — |
| 5 0 2 | 2.49 | 2.50 |
| 4 2 2 | 2.43 | — |
| 5 1 $\bar{2}$ | 2.38 | — |
| 4 3 $\bar{2}$ | 2.27 | — |
| 6 1 2 | 2.22 | 2.20 |
| 7 0 $\bar{2}$<br>5 3 2 | 2.10 | 2.10 |

TABLE I (*continued*).

| *h k l* | $d_{c.}$ | $d_{o.}$ | *h k l* | $d_{c.}$ | $d_{o.}$ |
|---|---|---|---|---|---|
| 6 2 $\bar{2}$ | 2.06 | — | 12 2 $\bar{2}$ | 1.33 | — |
| 5 4 $\bar{2}$ | 1.95 | — | 10 5 2 | 1.32 | — |
| 8 0 2 | 1.93 | — | 11 4 $\bar{2}$ | 1.30 | — |
| 7 2 2 | 1.90 | — | | | |
| 8 1 $\bar{2}$ | 1.85 | — | 1 1 3 | 2.17 | not meas. |
| 6 4 2 | 1.82 | — | 2 2 3 | 2.05 | not meas. |
| 7 3 $\bar{2}$ | 1.79 | — | 4 1 3 | 1.95 | 1.94 |
| 6 5 $\bar{2}$<br>9 1 2 | 1.71 | 1.73 | 3 3 3<br>5 2 3 | 1.89<br>1.79 | 1.87<br>1.77 |
| 8 3 2 | 1.67 | 1.66 | 4 4 3 | 1.72 | — |
| 10 0 $\bar{2}$ | 1.65 | 1.66 | 7 1 3 | 1.66 | 1.67 |
| 9 2 $\bar{2}$ | 1.63 | — | 6 3 3 | 1.63 | 1.62 |
| 7 5 2 | 1.59 | — | 5 5 3 | 1.56 | — |
| 8 4 $\bar{2}$ | 1.58 | — | 8 2 3 | 1.51 | — |
| 11 0 2 | 1.53 | — | 7 4 3 | 1.47 | — |
| 10 2 2 | 1.51 | — | 6 6 3 | 1.41 | — |
| 7 6 $\bar{2}$ | 1.50 | — | 10 1 3 | 1.40 | — |
| 11 1 $\bar{2}$<br>9 4 2 | 1.47 | — | 9 3 3<br>8 5 3 | 1.38<br>1.34 | —<br>— |
| 10 3 $\bar{2}$ | 1.45 | — | 11 2 3<br>7 7 3 | 1.28 | — |
| 8 6 2 | 1.41 | — | | | |
| 9 5 $\bar{2}$ | 1.40 | — | 10 4 3 | 1.25 | — |
| 12 1 2 | 1.38 | — | 9 6 3 | 1.21 | — |
| 11 3 2 | 1.36 | — | 13 1 3 | 1.19 | — |
| 13 0 $\bar{2}$<br>8 7 $\bar{2}$ | 1.34 | — | 12 3 3 | 1.17 | — |

The $(hkl)$ reflections with $-h+k+l \neq 3n$ and the reflections $(h0l)$ with $l \neq 2n$ being systematically absent, the choice of the space group is restricted to the $R\bar{3}c$ group or to its polar $R3c$ subgroup.

The intensity measurements were carried out for the zero and the 1st layer lines by the multiple film method; for the higher layer lines, owing to the remarkable enlargement of spots, we limited ourselves to record the qualitative course of the intensities.

## 2. – Structural considerations.

In analogy to what we summarized in the discussion of isotactic poly-alpha-butene and polystyrene structures, the monomeric units must necessarily repeat themselves, three by three, along the six threefold screw axes contained in the unit cell. Keeping into account the principle that the conformation of a polymeric chain in the crystalline state tends to be that of minimum potential energy which an isolated oriented chain would assume, since the effect of the neighbouring chains is generally small on its conformation, we tried first to build up the most probable model of the polymeric chain (Fig. 3). As second step, we studied the possible way of packing of such macromolecules, keeping into account the restrictions imposed by unit cell symmetry and size.

In Fig. 4 a small portion of the main chain is given, showing the details relative to the construction of the independent structural unit. Angles and bond lengths were deduced from literature data and from what we found in the structural study of analogous crystalline polymers [5]. The $\widehat{C_1C_2C_{1'}}$ and $\widehat{C_2C_1C_{1''}}$ angles were assumed as equal to 116° in order that the main chain atoms satisfy the principle of the staggered bonds.

To the $\widehat{C_1C_2C_3}$ and $\widehat{C_{1'}C_2C_3}$ angles was ascribed the tetrahedral value analogously with what we found for poly-alpha-butene [6]. In order to minimize the intramolecular contacts between the carbon atoms of the benzene ring and those of the polymeric chain, the most probable position of the benzene ring should be that in which the plane it defines bisects the $\widehat{C_1C_2C_{1'}}$ angle, at least until no consideration is taken of contacts due to fluorine atoms. As far as the independent structural unit is concerned there are two ortho non-equivalent positions, both possible

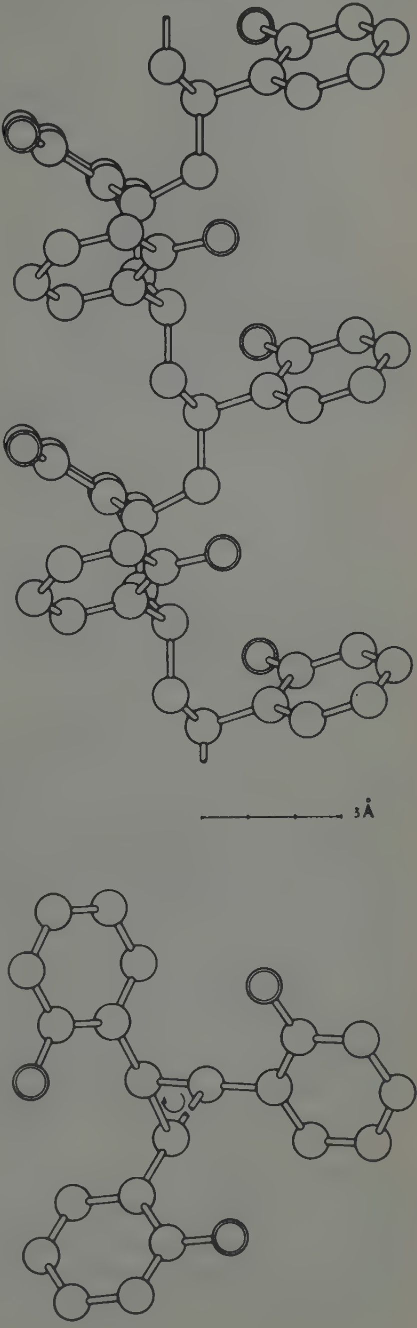


Fig. 3. – Conformation of the poly-ortho-fluorostyrene macromolecule (side and end views).

for the fluorine atom, say $F_4$ or $F_5$ (the index refers to the carbon atom to which the fluorine atom is linked).

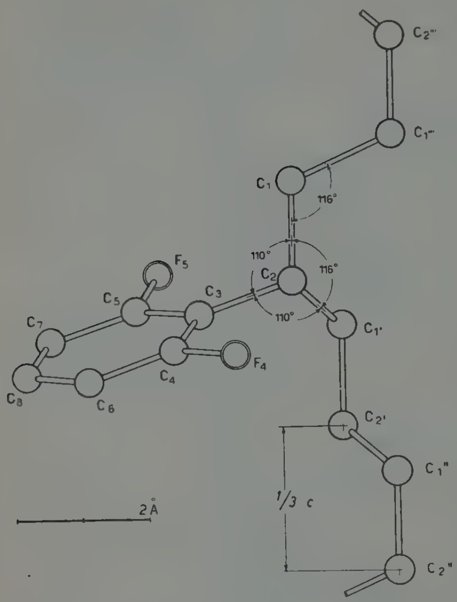


Fig. 4. – Conformation of the independent structural unit of poly-ortho-fluorostyrene ($C - C = 1.54$ Å, $(C - C)_{bz.} = 1.40$ Å, $C - F =$ $= 1.35$ Å, $\widehat{CCF} = 120°$).

Assuming as carbon-fluorine bond distance the value of literature [7], *i.e.* 1.35 Å, the Van der Waals contacts between fluorine atoms and the main chain carbon atoms result worse for the $F_5$ than for the $F_4$ position. Thus the position $F_5$ has to be rejected. The determination of the position assumed by the independent structural unit inside the unit cell, owing to the great structural analogy existing between poly-ortho-fluorostyrene and isotactic polystyrene, was made as for this latter, taking account of the particularly significant intensity of some equatorial reflections by means of structure factors graphs [8].

Moreover, we tried to have everywhere analogous Van der Waals contacts between the atoms of the neighbouring macromolecules.

The (220) and (660) reflections were first investigated, as for isotactic polystyrene, because of their outstanding intensity and because their structure factors do not vary with respect to the choice of the space group (*R3c* or *R3c*).

From Figs. 5, 6 it is possible to observe the position which must be given to the macromolecule in respect of the $x$ and $y$ axes, so as to justify the different ratio of intensity existing between the two reflections in the case of poly-ortho-fluorostyrene and polystyrene. In fact supposing that carbon atoms in poly-ortho-fluorostyrene have nearly equal positions in

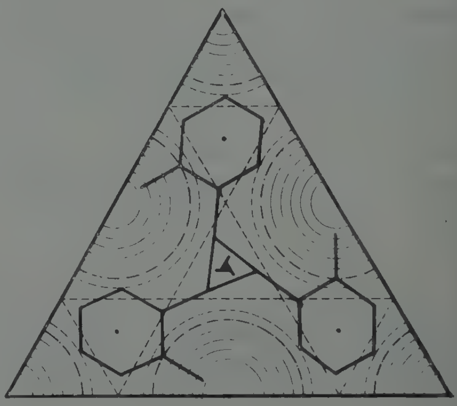


Fig. 5. – (220) structure factor graph, showing the position assumed by the macromolecule (contours are drawn at regular intervals: ——— positive lines; -·-·-· zero lines; –––– negative lines).

respect of the $x$ and $y$ axes, as in polystyrene, the fluorine atoms are in phase discordance with the carbon atoms for the (2 2 0) reflection and in accordance for the (6 6 0) reflection. Hence, it may be calculated, as found also experimentally, that F(6 6 0)/F(2 2 0) for poly-ortho-fluorostyrene is greater than the corresponding ratio for isotactic polystyrene.

Assuming the approximate position postulated for the macromolecule in order to satisfy the above assumptions, we have more precisely defined the coordinates of the independent structural unit taking into account the intermolecular contacts generated by rotating the macromolecule around its threefold screw axis. The calculations have been made first for the crystalline lattice defined by the $R3c$ space group, for which the packing of the macromolecules is independent of the choice of the origin in respect of the $z$ axis.

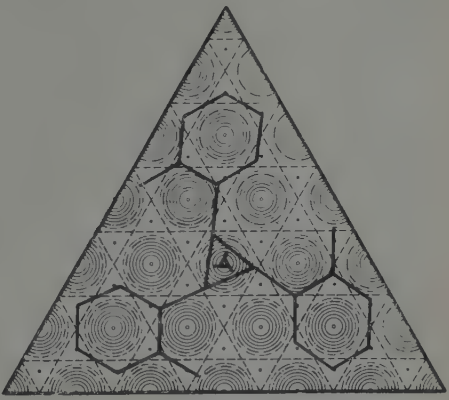


Fig. 6. (6 6 0) structure factor graph.

In Fig. 7 is reported the position which gives the best packing contacts between neighbouring macromolecules. For this position the contacts between carbon atoms are all in good accordance with the literature data and are homogeneous in all directions [9].

By rotating clockwise and anticlockwise the macromolecule by 2°, the contacts become fairly worse as it results from Table II. In the same table we

TABLE II. *Values of Van der Waals contacts between atoms of neighbouring macromolecules of poly-ortho-fluorostyrene. (Only the most significant values are reported).* (I): values calculated when the position assumed by the independent structural unit is that of Fig. 7. (II) and (III): values calculated by rotating the macromolecule by 2° anticlockwise and clockwise respectively.

| Atoms of isoclined molecules | | II Å | I Å | III Å | Atoms of anticlined molecules | | I Å |
|---|---|---|---|---|---|---|---|
| $C_{6A}$ | $C_{6C}$ | 3.45 | 3.54 | 3.60 | $C_{4A}$ | $C_{5C}$ | 3.44 |
| $C_{6A}$ | $C_{4C}$ | 3.46 | 3.56 | 3.64 | $C_{4A}$ | $C_{7C}$ | 3.51 |
| $C_{6A}$ | $F_C$ | 3.86 | 3.88 | 3.93 | $F_A$ | $C_{5C}$ | 3.28 |
| $C_{7A}$ | $C_{7B}$ | 3.58 | 3.50 | 3.43 | $F_A$ | $C_{7C}$ | 3.87 |
| $C_{7A}$ | $C_{5B}$ | 3.71 | 3.55 | 3.49 | $C_{5A}$ | $F_B$ | 3.25 |
| $C_{7A}$ | $C_{8B}$ | 3.58 | 3.45 | 3.34 | $C_{5A}$ | $C_{4B}$ | 3.40 |
| $F_A$ | $F_C$ | 3.43 | 3.44 | 3.46 | $C_{5A}$ | $C_{6B}$ | 3.56 |
| $F_A$ | $C_{4C}$ | 3.78 | 3.81 | 3.84 | $C_{8A}$ | $C_{6B}$ | 3.48 |
| $F_A$ | $C_{1C}$ | 3.53 | 3.58 | 3.63 | $C_{8A}$ | $C_{B}$ | 3.81 |

report the values of the intermolecular contacts if the space group were $R\bar{3}c$ (a suitable choice of the origin in respect of the $z$ axis is needed). In this case too, as for isotactic polystyrene and poly-alpha-butene, it is not possible to choose univocally the true space group, on the basis of the contacts only. It is possible, however, to remark that, although the distances of contacts do not diminish when enantiomorphous anticlined macromolecules face one another, the number of contacts increases remarkably.

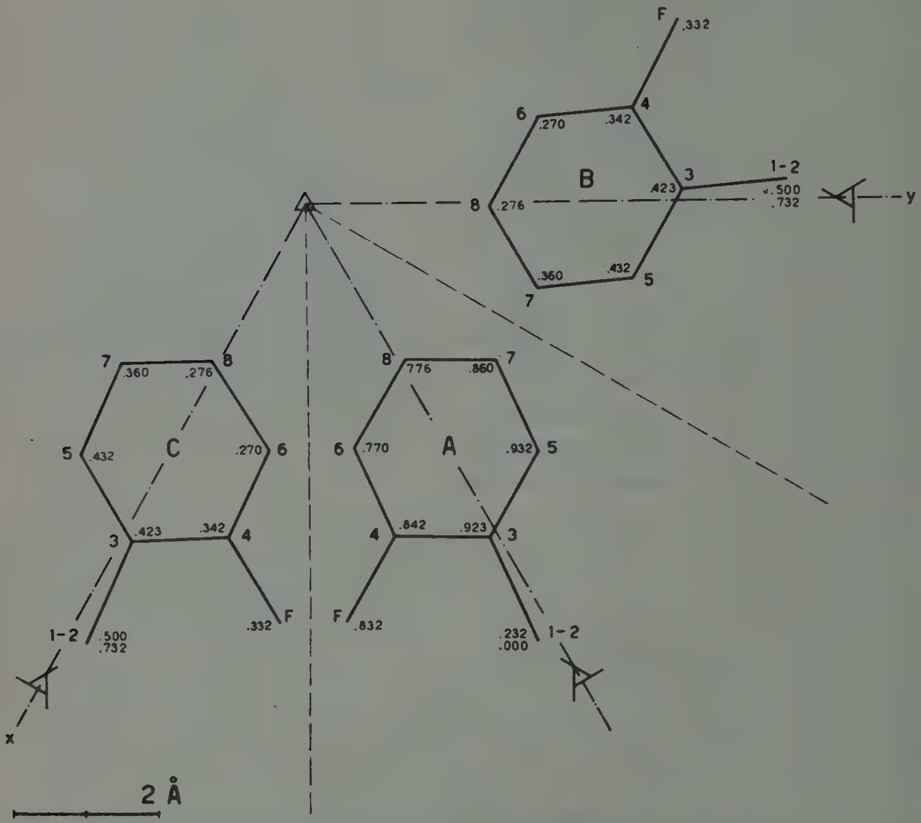


Fig. 7. – Actual position of the poly-ortho-fluorostyrene macromolecule in the unit cell.

## 3. – Calculation of structure factors.

We found it advisable also for poly-ortho-fluorostyrene, to make the calculation of the structure factors for both the space groups either according to the suggested model, or according to other trial models in which the monomeric unit was slightly rotated around the threefold screw axis or in which the plane of the benzene ring was slightly rotated around the $C_2C_3$ bond.

The best agreement between the observed and calculated structure factors (Table IV) was obtained for the non-centrosymmetric space group *R*3*c* using the co-ordinates reported in Table III, which nearly correspond to those of the model first postulated, with the exception of a rotation by 15° of the plane of the benzene ring around the $C_2C_3$ bond, from the position in which

TABLE III. – *Co-ordinates of the independent structural unit of poly-ortho-fluorostyrene.* (The atoms are marked as in Fig. 7).

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| $C_1$ | 0.306 | 0.293 | 0.232 |
| $C_2$ | 0.306 | 0.293 | 0.000 |
| $C_3$ | 0.238 | 0.231 | 0.923 |
| $C_4$ | 0.238 | 0.173 | 0.842 |
| $C_5$ | 0.176 | 0.233 | 0.932 |
| $C_6$ | 0.175 | 0.116 | 0.770 |
| $C_7$ | 0.114 | 0.176 | 0.860 |
| $C_8$ | 0.114 | 0.118 | 0.776 |
| F | 0.297 | 0.170 | 0.832 |

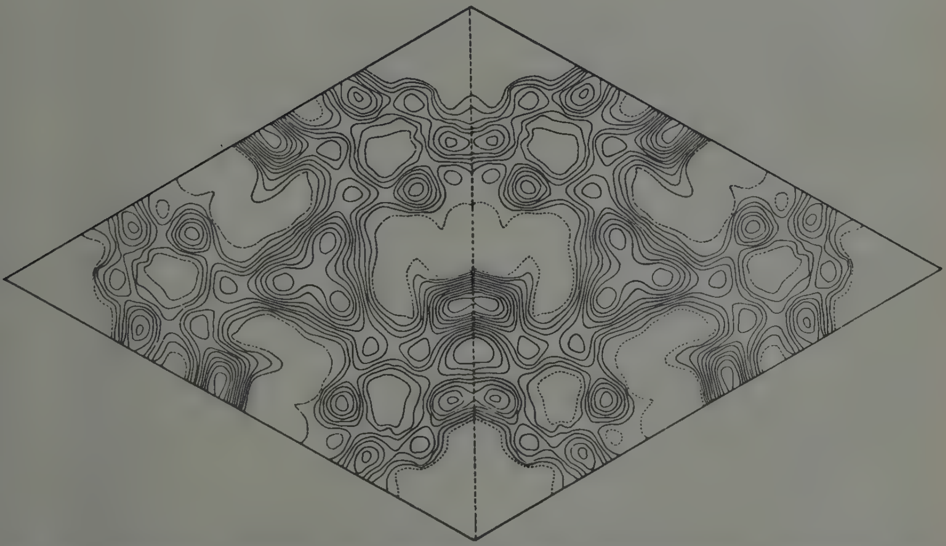


Fig. 8. – Projection on (001) of the electron density for poly-ortho-fluorostyrene, calculated for the *R*3*c* space group (levels in arbitrary units).

TABLE IV. - *Comparison between the observed and the calculated structure factors.* The $F_{o.}$ values correspond to the square root of the total intensity diffracted by the $(hkl)$ lattice plane, after effecting the usual corrections for the angular factors. In order to take into account the different multiplicity of the reflections, all the calculated structure factors, except the $(h00)$ and $(hh0)$ ones, were multiplied by $\sqrt{2}$; $B = 6$ Å$^2$. (Cu, K α).

| *h k l* | 2 sin ϑ | A | B | F$_{c.}$ | F$_{o.}$ | *h k l* | 2 sin ϑ | A | B | F$_{c.}$ | F$_{o.}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 1 0 | 0.139 | — 90 | — | 90 | 99 | 2 1 1 | 0.315 | —194 | +220 | 294 | 244 |
| 3 0 0 | 0.242 | — 3 | — 66 | 66 | 69 | 3 1 $\bar{1}$ | 0.372 | + 99 | + 95 | 137 | 152 |
| 2 2 0 | 0.279 | — 81 | — | 81 | 100 | 3 2 1 | 0.420 | —120 | —113 | 165 | 165 |
| 4 1 0 | 0.367 | — 64 | + 85 | 107 | 95 | 4 2 $\bar{1}$ | 0.485 | + 26 | + 43 | 51 | 108 |
| 3 3 0 | 0.418 | + 61 | — | 61 | 75 | 5 1 1 | 0.504 | +123 | + 27 | 126 | 148 |
| 6 0 0 | 0.483 | + 69 | — 26 | 74 | 55 | 4 3 1 | 0.541 | — 73 | — 6 | 74 | 72 |
| 5 2 0 | 0.502 | — 82 | — 77 | 113 | 86 | 6 1 $\bar{1}$ | 0.575 | + 5 | — 98 | 98 | 101 |
| 4 4 0 | 0.557 | + 57 | — | 57 | 60 | 5 3 $\bar{1}$ | 0.609 | + 42 | + 49 | 65 | 111 |
| 7 1 0 | 0.607 | + 4 | + 44 | 44 | 52 | 6 2 1 | 0.624 | + 18 | — 19 | 26 | — |
| 6 3 0 | 0.638 | + 61 | + 37 | 71 | 84 | 5 4 1 | 0.670 | — 15 | + 36 | 39 | 43 |
| 5 5 0 | 0.696 | — 53 | — | 53 | 46 | 7 2 $\bar{1}$ | 0.698 | — 45 | — 12 | 47 | 37 |
| 9 0 0 | 0.722 | — 2 | — 56 | 56 | 42 | 8 1 1 | 0.724 | + 18 | + 37 | 41 | — |
| 8 2 0 | 0.736 | + 33 | — 10 | 34 | — | 6 4 $\bar{1}$ | 0.738 | — 60 | — 11 | 61 | 55 |
| 7 4 0 | 0.775 | — 26 | — 40 | 48 | 50 | 7 3 1 | 0.752 | + 94 | — 57 | 110 | 147 |
| 6 6 0 | 0.835 | — 85 | — | 85 | 101 | 6 5 $\bar{1}$ | 0.803 | — 78 | — 3 | 91 | 105 |
| 10 1 0 | 0.846 | + 14 | + 30 | 33 | — | 9 1 $\bar{1}$ |  | — 45 | + 15 |  |  |
| 9 3 0 | 0.869 | + 19 | — 25 | 31 | — | 8 3 $\bar{1}$ | 0.825 | + 3 | — 66 | 66 | 43 |
| 8 5 0 | 0.912 | + 11 | + 36 | 38 | 54 | 9 2 1 | 0.847 | — 17 | — 30 | 34 | — |
| 12 0 0 | 0.965 | — 1 | — 25 | 25 | — | 7 5 $\bar{1}$ | 0.871 | — 9 | + 50 | 51 | — |
| 11 2 0 | 0.974 | — 13 | + 14 | 41 | 44 | 8 4 1 | 0.881 | + 38 | + 62 | 73 | 82 |
| 7 7 0 |  | + 36 | — |  |  | 10 2 $\bar{1}$ | 0.923 | — 16 | + 13 | 21 | — |
| 10 4 0 | 1.004 | + 6 | — 10 | 12 | — | 7 6 1 | 0.934 | + 11 | — 42 | 44 | — |
| 9 6 0 | 1.050 | — 6 | — 17 | 18 | — | 11 1 1 | 0.958 | + 26 | — 2 | 39 | 46 |
| 13 1 0 | 1.088 | + 8 | + 22 | 24 | — | 9 4 $\bar{1}$ |  | + 25 | + 14 |  |  |
| 12 3 0 | 1.105 | — 19 | — 15 | 24 | — | 10 3 1 | 0.976 | — 31 | + 22 | 38 | — |
| 8 8 0 | 1.114 | — 8 | — | 8 | — | 8 6 $\bar{1}$ | 1.008 | — 20 | + 1 | 20 | — |
| 11 5 0 | 1.140 | + 7 | — 4 | 8 | — | 9 5 1 | 1.014 | — 21 | — 8 | 22 | — |
| 10 7 0 | 1.188 | + 24 | + 13 | 27 | — | 12 1 $\bar{1}$ | 1.035 | — 28 | — 43 | 51 | 51 |
| 15 0 0 | 1.206 | — 28 | — 21 | 53 | 42 | 11 3 $\bar{1}$ | 1.049 | + 32 | + 6 | 32 | — |
| 14 2 0 | 1.213 | — 38 | + 13 |  |  | 8 7 1 | 1.070 | + 16 | — 3 | 16 | — |
| 13 4 0 | 1.238 | + 15 | + 14 | 20 | — | 12 2 1 | 1.079 | — 45 | — 6 | 46 | vvw |
| 9 9 0 | 1.252 | + 1 | — | 1 | — | 10 5 $\bar{1}$ | 1.085 | + 5 | — 14 | 15 | — |
| 12 6 0 | 1.275 | — 23 | — 10 | 25 | — | 11 4 1 | 1.101 | + 2 | — 25 | 25 | — |
| 16 1 0 | 1.328 | + 70 | + 11 | 71 | 44 | 9 7 $\bar{1}$ | 1.141 | — 13 | — 11 | 17 | — |
| 11 8 0 |  | — 1 | + 8 |  |  | 10 6 1 | 1.150 | + 45 | + 7 | 46 | — |
| 15 3 0 | 1.343 | — 29 | — 28 | 40 | — | 13 2 $\bar{1}$ | 1.159 | + 59 | + 22 | 63 | vvw |
| 14 5 0 | 1.372 | + 2 | + 4 | 5 | — | 12 4 $\bar{1}$ | 1.184 | — 14 | + 10 | 17 | — |
| 10 10 0 | 1.391 | + 10 | — | 10 | — | 14 1 1 | 1.193 | — 49 | + 62 | 79 | vvw |
| 13 7 0 | 1.413 | + 13 | + 5 | 14 | — | 13 3 1 | 1.206 | — 5 | + 1 | 14 | — |
| 18 0 0 | 1.447 | + 23 | — 18 | 40 | 50 | 9 8 1 |  | — 12 | — 6 |  |  |
| 17 2 0 | 1.453 | — 6 | + 27 |  |  | 11 6 $\bar{1}$ | 1.224 | + 19 | + 13 | 23 | — |
|  |  |  |  |  |  | 12 5 1 | 1.233 | — 26 | — 1 | 26 | — |

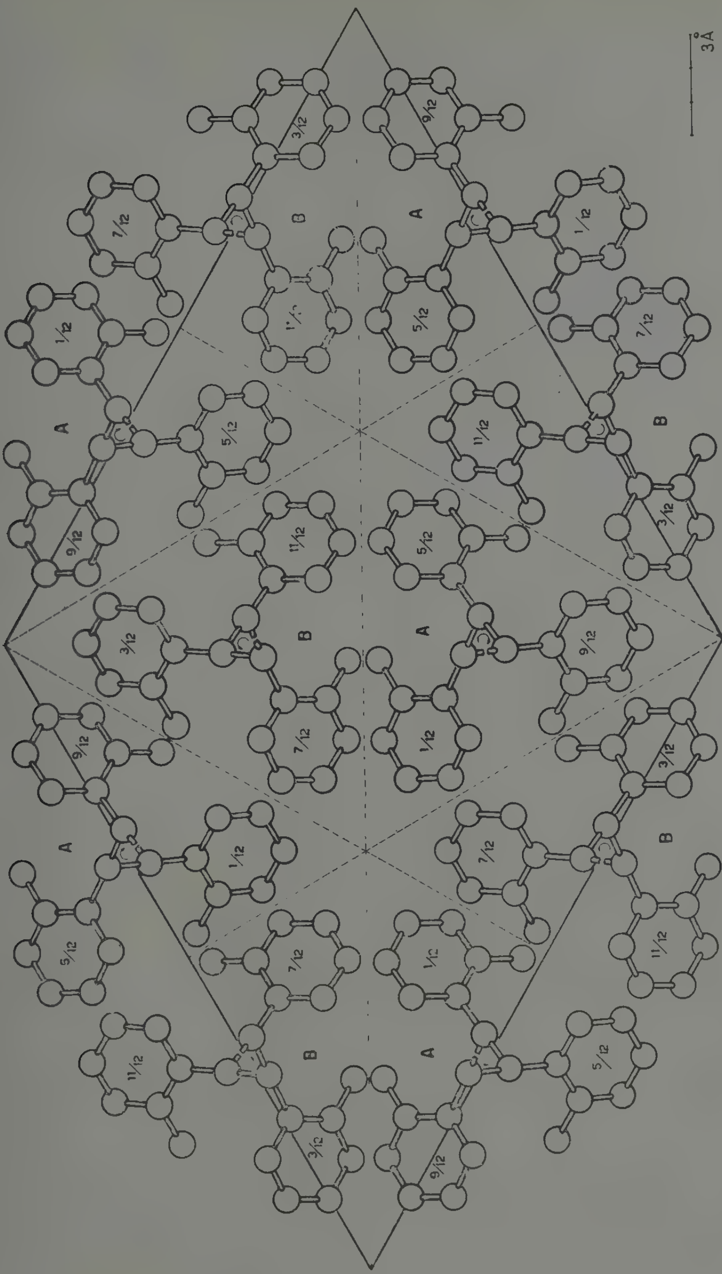


Fig. 9. – Projection on (0 0 1) of the unit cell content of poly-ortho-fluorostyrene ($R3c$ space group).

it bisects the $\widehat{C_1C_2C_{1'}}$ angle. Following the knowledge of the phase angles of the $(hk0)$ reflections (the $R3c$ space group is a non-centrosymmetric one) it was possible to make a Fourier projection of the electron density on the (0 0 1) plane. The Fourier projection has given a good evidence of the rotation of the plane of the benzene ring in respect of the plane which bisects the $\widehat{C_1C_2}C_{1'}$ angle. The coherent values assumed by the electron density in the points corresponding to the postulated positions of the atoms and the lack of spurious maxima, as given in Fig. 8, enable us to believe in the substantial exactness of the suggested model. In Fig. 9 and Fig. 10 a comparison between the structure of the examined polymer and that found for isotactic polystyrene is given.

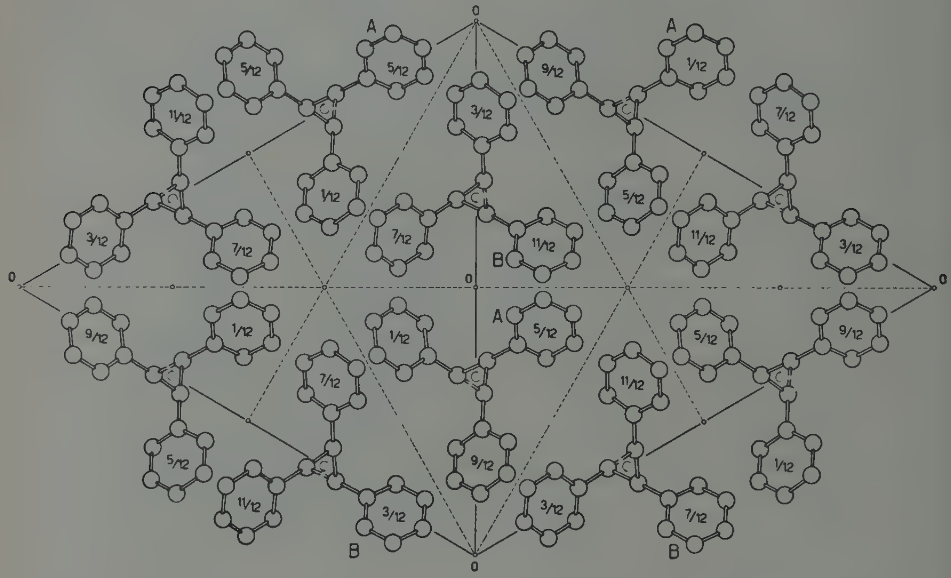


Fig. 10. – Projection on (001) of the structure of isotactic polystyrene for the *R3c* space group.

The analogy results quite fair between the structures of the two polymers, which determines the possibility, experimentally proved by us [10], to obtain crystalline copolymers of styrene and orthofluorostyrene.

The fact that, as reported above, the plane of the benzene ring appears to be rotated by 15° around the $C_2C_3$ bond, from the position in which it bisects the $\widehat{C_1C_2}C_{1'}$ angle (as it occurs for polystyrene) may be easily explained in order to diminish the contact between $F_4$ and $C_{1''}$ (Fig. 4).

Such a rotation also takes place for other polymers of ortho-substituted styrenes as poly-ortho-methylstyrene, even when the shape of the main chain is slightly different from the threefold helix one.

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SUPPLEMENTO AL VOLUME XV, SERIE X
DEL NUOVO CIMENTO

N. 1, 1960
1° Trimestre

# Crystal Structure of Poly-ortho-Methylstyrene.

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(ricevuto il 26 Giugno 1959)

In precedent papers [1] evidence was given which enabled us to establish the helix chain conformation of many isotactic polymers. The crystal structure of some polymers was studied with more detail, whose chain shows a threefold helix conformation as that of polypropylene, poly-alpha-butene and polystyrene [2]. Other forms of chain were qualitatively discussed in terms of Fourier transforms [3]. Aim of this work is the determination of the structure of an isotactic polymer, prepared by means of highly stereospecific catalysts obtained reacting titanium halides with alkylaluminum compounds [4], the poly-ortho-methylstyrene, whose chain conformation is that of a fourfold helix.

## 1. – Experimental.

Oriented fibers were obtained, according to methods similar to those used for polystyrene [5], hot-annealing under tension a small cylinder of poly-ortho-methylstyrene extruded from the melt. The fiber spectra that we have obtained show many reflections. The orientation of the crystals is however worse than that which may be obtained for the other polymers previously studied by us. By reciprocal lattice methods [6] it was possible to reconstruct the unit cell of the polymer under examination. All the reflections may be readily indexed for a tetragonal unit cell with $a = b = 19.01$ Å; $c = 8.1$ Å (within $\pm 1\%$). Owing to the systematic absence of the reflections $hkl$ with $h+k+l = 2n+1$, $0kl$ with $l = 2n+1$, $hhl$ with $2h+l = 4n+2$, we were able to conclude that the space group is $I4_1cd$.

To make an example, the agreement between the observed and calculated Bragg distances for $hk0$ reflections is shown in Table I.

TABLE I. – *Comparison between the observed and calculated Bragg distances* d($hk0$) *of poly-ortho-methylstyrene.* (Cu, K$\alpha$)

| $2\theta$ | $hk0$ | $d_{o.}$ | $d_{c.}$ |
|---|---|---|---|
| 9.3 | 200 | 9.500 | 9.505 |
| 13.00 | 220 | 6.815 | 6.720 |
| 14.80 | 310 | 5.990 | 6.010 |
| 20.80 | 420 | 4.270 | 4.250 |
| 24.00 | 510 | 3.710 | 3.730 |
| 28.10 | 600 | 3.170 | 3.170 |
| 33.40 | 640 | 2.683 | 2.688 |
| 36.10 | 730 | 2.488 | 2.496 |
| 42.60 | 840 | 2.122 | 2.125 |
| 47.90 | 10 00–860 | 1.899 | 1.901 |

The space group allows the presence of 16 equivalent structural units in the unit cell, and in fact, should we assume that 16 monomeric units are contained in the unit cell, the density is calculated to be 1.07 g/cm$^3$, in good agreement with the experimental value. The chain is necessarily expected to assume a fourfold helix conformation; the macromolecules are isoclined and, through the operation of glide planes with translation parallel to $c$, each right handed helical chain is surrounded by four left-handed chains and viceversa.

## 2. – Chain shape and crystal structure.

The first trials, which aimed at establishing the structure, were made by utilizing the principles that we summarized in a preceding work of ours [7]. The identity period along the fourfold screw axis (8.1 Å) allows, by itself, to fancy the most probable conformation of the chain if for the length of the C—C bond the value of 1.54 Å and for the $\widehat{\mathrm{CCC}}$ angles tetrahedral values are assumed (Figs. 1 and 2).

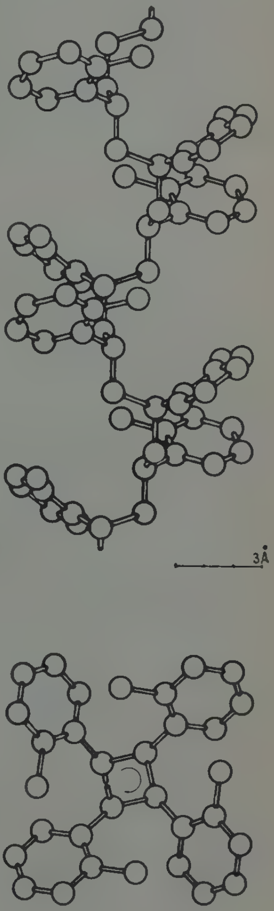

Fig. 1. – Conformation of the poly-ortho-methylstyrene macromolecule in the crystal state (side and end views).

In analogy to what we found for polystyrene, the plane of the benzene ring was placed first to bisect the $C_1\widehat{C_2}C_1'$ angle. However, as we shall further see, the best agreement between experimental and calculated intensities was obtained for the conformation drawn in Fig. 2, in which the benzene plane forms an angle of 8° with the plane which bisects the $C_1\widehat{C_2}C_1'$ angle. The $C_9$ methyl group was bound to $C_8$ instead of $C_4$ in order to get better intramolecular Van der Waals contacts; actually, should it be bound to $C_4$, we would have had a $C_9$—$C_1$ contact shorter than 3.0 Å, which is most unlike from a stereochemical viewpoint.

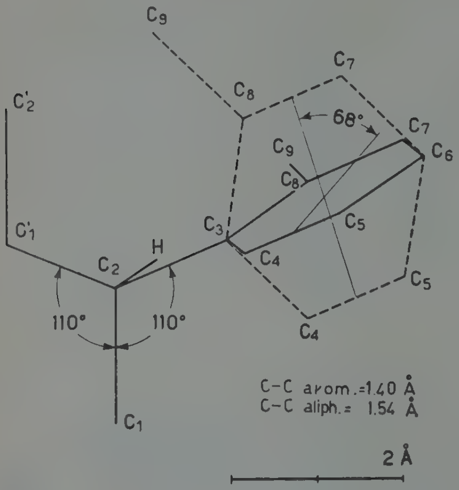

Fig. 2. – Model of a monomeric unit with specified angles and distances.

The problem of determining the structure was faced, still with reference to the preliminary conformation, taking into account stereochemical considerations concerning the mode of packing between neighbouring macromolecules, and examining the value of some appropriately chosen structure factors.

In the diagram of Fig. 3 the course of the closest Van der Waals contacts is sketched as a function of the angle $\varphi$ that may be assumed by the macromolecule, supposed to rotate around the fourfold screw axis. (The value of $\varphi$ is referred to the angle formed by the axis *b* with the line joining the center of the chain to $C_6$). As it may be observed from this diagram, for $\varphi = 57°.5$ a position exists in which the best packing contacts with neighbouring

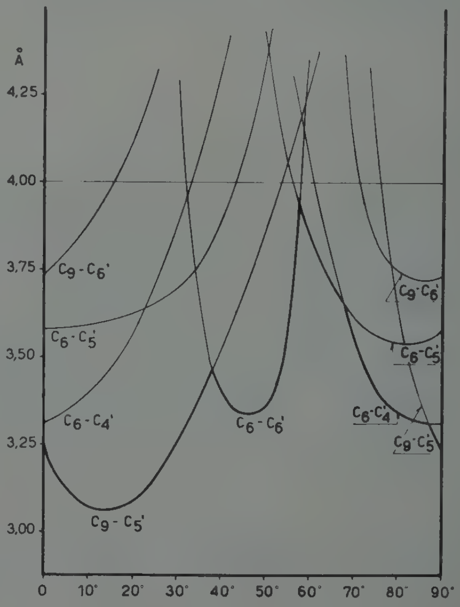

Fig. 3. – Van der Waals contacts between neighbouring molecules, according to the position $\varphi$ which could be assumed by the molecule around the four-fold screw axis.

« symmetry-related » macromolecules are obtained. In fact the lowest distances between aromatic carbon atoms, recorded in literature, are comprised within 3.4 and 3.7 Å; for $\varphi = 57°.5$ the values of the observed contacts are all greater than 3.8 Å and suggest that for this position one can obtain the best filling of space.

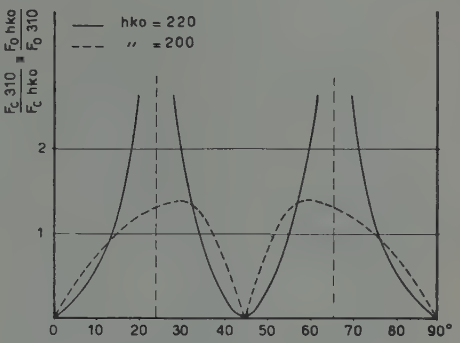

Fig. 4. – Values of the ratios $(F_{c.}(h k 0)/F_{c.}(h'k'0))\cdot(F_{o.}(h'k'0)/F_{o.}(h k 0))$ according to the position $\varphi$ which could be assumed by the molecule around the four-fold screw axis.

This result has been further confirmed by a study of the behaviour of the values of the structure factors of the most important reflections ever plotted as a function of the angle $\varphi$. A very good agreement between calculated ($F_{c.}$) and observed ($F_{o.}$) does exist for $\varphi$ values of about 57°. As an example we report in Fig. 4 a diagram illustrating the calculated behaviour of the expressions

$$\frac{F_{c.}(h\,k\,0)}{F_{c.}(h'k'0)}\cdot\frac{F_{o.}(h'k'0)}{F_{o.}(h\,k\,0)}\,.$$

for three typical $h\,k\,0$ reflections. The chosen reflections correspond to high Bragg distances so that they are sensitive to the orientation of the macromolecule but not to small variations of its conformation. Since the above reported expression needs to be equal to 1 in a ideally perfect structure, the positions which may be assumed are very limited, and one among these falls at $\approx 57°$.

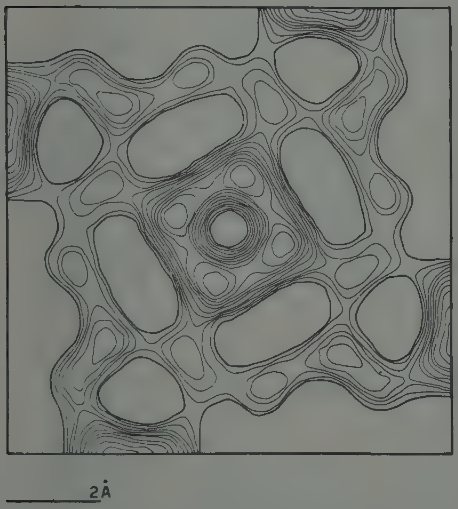

Fig. 5. – Fourier projection of the electron density on the (001) plane (arbitrary units).

It was possible to obtain a further improvement of the structure by searching for the model that might better correspond to the image given by a Fourier projection of the electronic density (Fig. 5) whose phases resulted univocally determined from the choice of the approximate orientation of the macromolecule.

For instance a clear evidence was obtained, that the plane of the ben-

TABLE II. – *Co-ordinates of the independent structural unit of poly-ortho-methylstyrene.*

| | $x/a$ | $x/b$ | $z/c$ |
|---|---|---|---|
| $C_1$ | .197 | .270 | .810 |
| $C_2$ | .197 | .270 | .000 |
| $C_3$ | .136 | .314 | .066 |
| $C_4$ | .133 | .383 | .042 |
| $C_5$ | .077 | .423 | .100 |
| $C_6$ | .024 | .395 | .184 |
| $C_7$ | .027 | .325 | .205 |
| $C_8$ | .083 | .285 | .146 |
| $C_9$ | .086 | .209 | .174 |

TABLE III. – *Comparison between the observed and calculated structure factors of poly-ortho-methylstyrene.*

The $F_{o.}$ values correspond to the square root of the total intensity diffracted by the general $(h\,k\,l)$ lattice plane after effecting the corrections for the usual angular factors. In order to take into account the different multiplicity of the reflections, the $F(h\,h\,0)$ and $F(h\,0\,0)$ calculated structure factors were divided by $\sqrt{2}$:

| $h\,k\,0$ | $F_{c.}$ | $F_{o.}$ | $h\,k\,1$ | $F_{c.}$ | $F_{o.}$ | $h\,k\,2$ | $F_{c.}$ | $F_{o.}$ |
|---|---|---|---|---|---|---|---|---|
| 2 0 0 | 150 | 181 | 2 1 1 | 239 | 206 | 1 1 2 | 183 | not meas. |
| 2 2 0 | 85 | 96 | 3 2 1 | 99 | 148 | 2 0 2 | 211 | 194 |
| 3 1 0 | 201 | 175 | 4 1 1 | 191 | 201 | 3 1 2 | 99 | 97 |
| 4 0 0 | 49 | — | 4 3 1 | 91 | 163 | 4 0 2 | 77 | — |
| 4 2 0 | 99 | 86 | 5 2 1 | 65 | 73 | 3 3 2 | 171 | 171 |
| 5 1 0 | 33 | 74 | 6 1 1 | 40 | — | 4 2 2 | | |
| 4 4 0 | 2 | — | 5 4 1 | 11 | — | 5 1 2 | 90 | 103 |
| 5 3 0 | 11 | — | 6 3 1 | 92 | 83 | 5 3 2 | 87 | 113 |
| 6 0 0 | 91 | 95 | 7 2 1 | 11 | — | 6 0 2 | | |
| 6 2 0 | 34 | — | 6 5 1 | 39 | 79 | 6 2 2 | 106 | 118 |
| 7 1 0 | 93 | 113 | 8 1 1 | 71 | 88 | 7 1 2 | 38 | — |
| 6 4 0 | 60 | — | 7 4 1 | | | 5 5 2 | | |
| 7 3 0 | 128 | 134 | 8 3 1 | 41 | — | 6 4 2 | 95 | 135 |
| 8 0 0 | 57 | — | 9 2 1 | 121 | 101 | 7 3 2 | 86 | — |
| 8 2 0 | 10 | — | 7 6 1 | | | 8 0 2 | 73 | — |
| 6 6 0 | 55 | — | 8 5 1 | 73 | — | 8 2 2 | 30 | — |
| 7 5 0 | 25 | — | 9 4 1 | 93 | — | 7 5 2 | 86 | — |
| 8 4 0 | 100 | 131 | 10 1 1 | 27 | — | 8 4 2 | 48 | — |
| 9 1 0 | 27 | — | 10 3 1 | 61 | — | 9 1 2 | 24 | — |
| 9 3 0 | 52 | — | 8 7 1 | 27 | — | 9 3 2 | 34 | — |
| 10 0 0 | 207 | 169 | 9 6 1 | 61 | — | 7 7 2 | 52 | — |
| 8 6 0 | | | 11 2 1 | 82 | 82 | 10 0 2 | 86 | 96 |
| 10 2 0 | 13 | — | 10 5 1 | | | 8 6 2 | | |
| 9 5 0 | 68 | — | 11 4 1 | 41 | — | 10 2 2 | 55 | — |

zene ring forms an angle of 68° with the $C_1C_2C_3$ plane of Fig. 2. This angle resulted of 60° for polystyrene and in fact the $C_4$ and $C_8$ atoms were thus equidistant from $C_1$ and $C'_1$. However, with an angle of 60° we would have had a too close contact between $C_9$ and $C'_2$. An analogous effect was noticed for poly-ortho-fluorostyrene [8], where the plane of benzene does not bisect the $\widehat{C_1C_2C'_1}$ angle being displaced of about 15° from the bisecting plane.

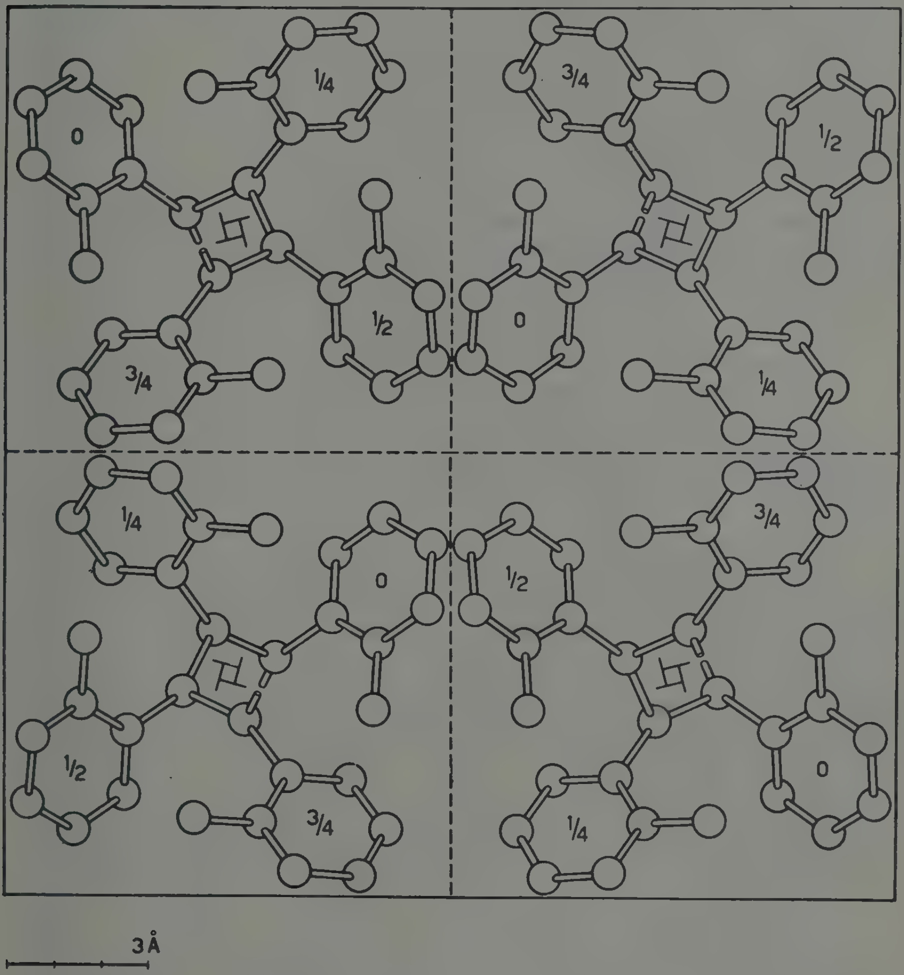

Fig. 6. – Model of the structure of poly-ortho-methylstyrene on (001).

By means of the found co-ordinates, given in Table II, a complete calculation of the structure factors was made, thus finding a good agreement between experimental and calculated structure factors for the $hk0$, $hk1$, $hk2$ reflections (Table III). This enables us to believe that the structure (Fig. 6) is sufficiently determined, within the limits of the experimental data. For the structure factors of this compound we did not bring any correction due to thermal movements. In fact it was impossible to perform the observation of reflections having values of $2 \sin \vartheta$ higher than 1.0, owing to the blackening of the film and the progressive enlargement of diffraction spots. For a structure of this type, characterized by a high degree of order, a relatively low thermal factor may be reasonably expected, probably of the order of 4 Å², and thus practically without affecting the structure factors in the angular region under consideration.

## 3. – Final considerations.

Apart from the different symmetry of the helix it is evident from Fig.s 6 and 7 that a close analogy exists between the structure and the mode of packing of this compound with the structure and the mode of packing of poly-ortho-fluorostyrene, which belongs to the polar space group of the rhombohedral system (*R3c*), correspondent to the polar space group of the tetragonal system $I4_1cd$.

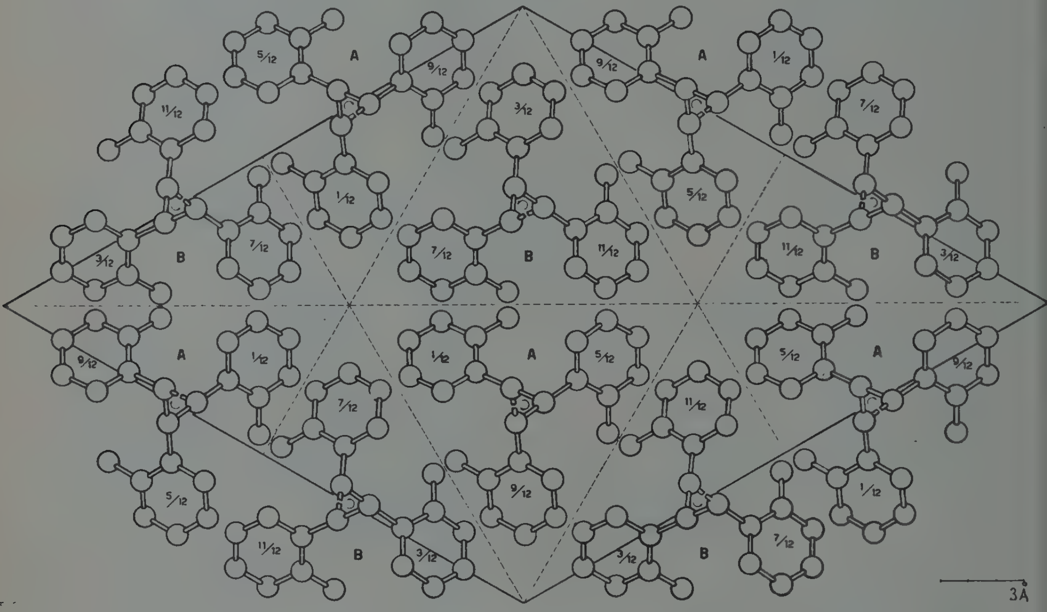

Fig. 7. – Model of the structure of poly-ortho-fluorostyrene on (001).

The typical shape of the chain of poly-ortho-methylstyrene, has been already discussed by us [3] and corresponds to the $(AB')_4$ type, according to the terminology introduced by Bunn, which was slightly modified by us. The angles of internal rotation along carbon-carbon bonds along the chain are alternately of 180° (A) and 90° (B′) instead of 180° (A) and 60° (B) as it happens with poly-ortho-fluorostyrene and polystyrene. This fact is due to the bulkiness of the methyl group, in comparison with fluorine or hydrogen atoms.

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SUPPLEMENTO AL VOLUME XV, SERIE X
DEL NUOVO CIMENTO

N. 1, 1960
1° Trimestre

# Crystal Structure of Poly-alpha-Vinylnaphtalene.

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(ricevuto il 26 Giugno 1959)

In the present work we shall briefly refer on the crystal structure of isotactic poly-alpha-vinylnaphtalene, prepared by means of highly stereospecific catalysts obtained reacting titanium halides with alkylaluminum compounds [1], which presents many analogies with the structure of poly-ortho-methylstyrene that we have already determined [2].

Fibers of the polymer are obtained by hot-extrusion and annealing under tension, which allow them to crystallize and to become oriented. When compared with spectra given by other isotactic polymers, the fiber spectra of poly-alpha-vinylnaphtalene shows a worse orientation, although the detectable reflections are numerous enough for a structural determination.

We were able to identify the space group to which the polymer belongs using, as usual, the reciprocal lattice methods that are illustrated in some preceding works of ours [3]. The best agreement between the observed and calculated Bragg distances was found for a tetragonal unit cell whose identity periods are: $a = b = 21.20$ Å; the value of $c$ (chain axis) precedently found [4] is 8.10 Å (all values within 1% accuracy).

The space group is, as for isotactic poly-ortho-methylstyrene, $I4_1cd$, being systematically absent the reflections $hkl$ with $h+k+l \neq 2n$, $hhl$ with $2h+l \neq 4n$ and $0kl$ with $l \neq 2n$.

In Table I the agreement between observed and calculated Bragg distances, is given, as an example, for the $hk0$ reflections.

The presence in the $I4_1cd$ space group of fourfold screw axes and the presence in the unit cell of 16 monomeric units (a reliable density value is thus calculated (1.12 g/cm³)) requires that the macromolecular chain has the symmetry of a fourfold helix. It is then needed that along the chain axis (8.10 Å) exactly four monomeric units are arranged.

TABLE I. – *Comparison between observed and calculated Bragg distances* $d(hk0)$ *of poly-alpha-vinylnaphtalene.* (Cu, Kα).

| $2\theta$ | $kh0$ | $d_{o.}$ | $d_{c.}$ |
|---|---|---|---|
| 8.25 | 200 | 10.720 | 10.600 |
| 11.50 | 220 | 7.595 | 7.495 |
| 13.22 | 310 | 6.705 | 6.704 |
| 18.60 | 420 | 4.770 | 4.740 |
| 23.55 | 440 | 3.787 | 3.748 |
| 25.20 | 600 | 3.522 | 3.533 |
| 31.80 | 730 | 2.805 | 2.783 |
| 34.50 | 820 | 2.607 | 2.571 |
| 36.15 | 750 | 2.481 | 2.464 |
| 38.45 | 910 | 2.356 | 2.341 |
| 40.36 | 930 | 2.250 | 2.234 |
| 42.57 | 10 00 | 2.113 | 2.122 |
| 42.57 | 860 | 2.113 | 2.122 |
| 46.09 | 10 40 | 1.981 | 1.968 |
| 50.16 | 10 60 | 1.834 | 1.817 |
| 52.11 | 11 50 | 1.734 | 1.754 |
| 54.69 | 10 80 | 1.682 | 1.676 |

TABLE II. – *Co-ordinates of the independent structural unit of poly-alpha-vinylnaphtalene.*

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| $C_1$ | .201 | .265 | .657 |
| $C_2$ | .201 | .265 | .843 |
| $C_3$ | .149 | .310 | .907 |
| $C_4$ | .147 | .372 | .881 |
| $C_5$ | .096 | .409 | .939 |
| $C_6$ | .051 | .384 | .022 |
| $C_7$ | .053 | .321 | .047 |
| $C_8$ | .102 | .286 | .990 |
| $C_9$ | .105 | .223 | .013 |
| $C_{10}$ | .057 | .198 | .095 |
| $C_{11}$ | .007 | .234 | .153 |
| $C_{12}$ | .005 | .296 | .128 |

As for poly-ortho-methylstyrene all the macromolecules belonging to the same crystal are isoclined and related to the neighbouring ones by means of glide planes with translation of $c/2$ so that each right or left-handed chain is surrounded by four left or right-handed chains respectively.

Owing to the known periodicity along the $c$ axis and the fourfold helix symmetry of the chain, it is possible to build up univocally an approximate model of the main chain, satisfying the conditions that the C—C distances be 1.54 Å and the $\widehat{CCC}$ valence angles be tetrahedral. The plane of the naphtalene ring, in accordance with what was found in the study of poly-ortho-methylstyrene [2], was so oriented in order to determine the best intramolecolar contacts between atoms of the same chain, and therefore, in a position slightly displaced from the plane bisecting the $\widehat{C_1C_2C'_1}$ angle (Fig. 1). The atoms $C_9$ and $C_{12}$ have been linked to $C_8$ and $C_7$, respectively (see Fig. 1), but not to $C_4$ and $C_5$ in order to avoid sterical hindrance between $C_9$ and $C'_1$ atoms. On the basis of such a model the structural investigation was carried out. (In Figs. 1 and 2 we have drawn, for the sake of simplicity, the actual macromolecule conformation obtained after the usual refinements, which is slightly different from the first postulated model).

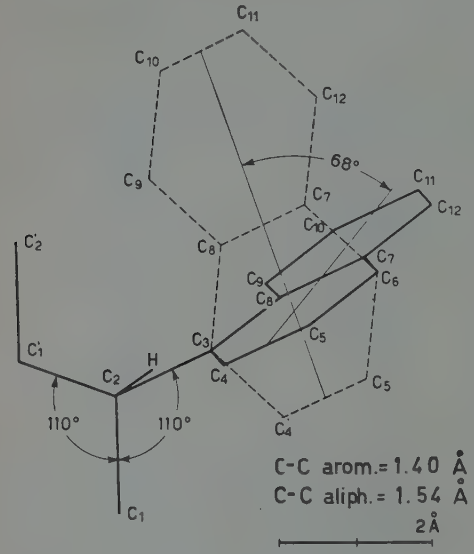

Fig. 1. – Model of a monomeric unit with specified angles and distances.

As for poly-ortho-methylstyrene we have analysed the course of the contacts between neighbouring macromolecules and the values which may be assumed by the structure factors as a function of the possible orientations of the macromolecule around the fourfold screw

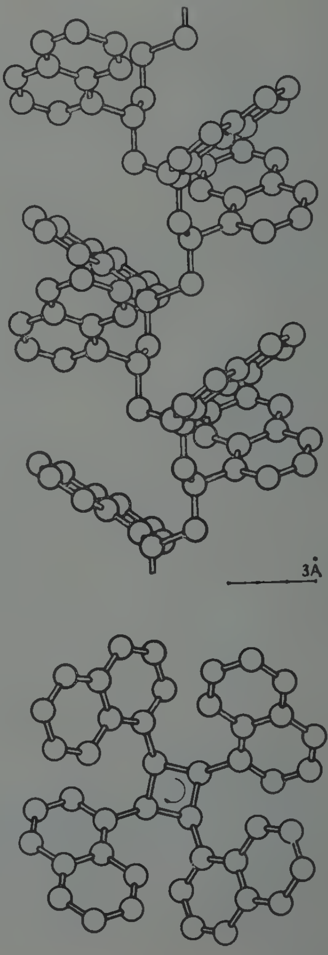

Fig. 2. – Conformation in the crystal state of the poly-alpha-vinylnaphtalene macromolecule (side and end views).

axis. The orientation is expressed by the angle $\varphi$ formed by the line joining the centre of the chain with $C_6$ and the $b$ axis.

In Fig. 3 a plot is recorded which shows the variations of the Van der Waals contacts as a function of the above defined $\varphi$ rotation angle.

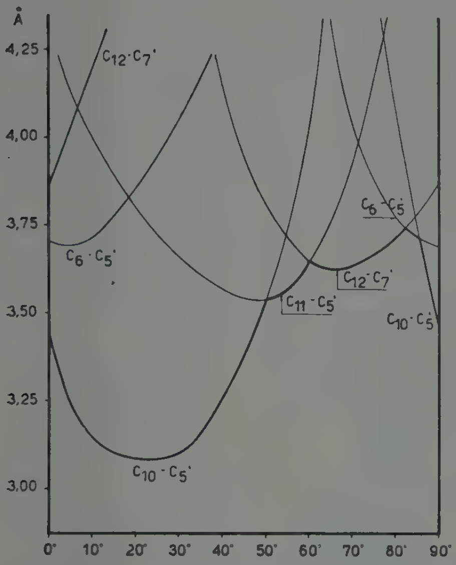

Fig. 3. – Van der Waals contacts between neighbouring molecules according to the possible position $\varphi$ assumed by the molecule around the four-fold screw axis.

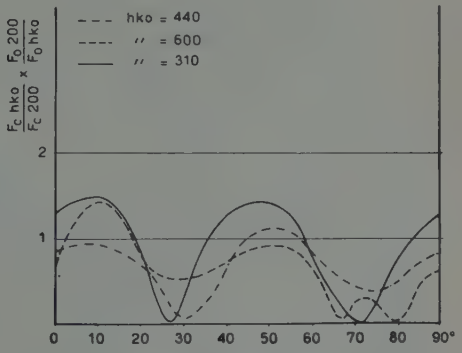

Fig. 4. – Values of the ratios $(F_{c.}(k\,h\,0)/$ $/F_{c.}(h'k'0))\cdot(F_{o.}(h'k'0)/F_{o.}(h\,k\,0))$ according to the possible position $\varphi$ assumed by the molecule around the four-fold screw axis.

If one assumes as minimum values of the distances between aromatic carbon atoms $(3.4 \div 3.7)$ Å, possible values of $\varphi$ seem to be all those comprised within $\varphi = 50°$ and $\varphi = 85°$. The range of possible values of $\varphi$ does not seem strongly delimited as in the case of poly-ortho-methylstyrene by these considerations only.

From the behaviour of the calculated structure factors of the most significant reflections with the angle of trial rotation $\varphi$ the conclusion was drawn that the best accordance between experimental and calculated structure factors is obtained for $\varphi = 55° \pm 5°$.

As an example, in Fig. 4, the course versus $\varphi$ of some ratios

$$\frac{F_{c.}(h\,k\,0)}{F_{c.}(h'k'0)}\cdot\frac{F_{o.}(h'k'0)}{F_{o.}(h\,k\,0)},$$

is recorded. It is clearly noticeable that around 55° there is the best approximation of the studied ratios to unitary values that should arise from an ideally perfect accordance. This notwithstanding, we have also studied the possibility that, according to the behaviour of the contacts illustrated in Fig. 3, the value of $\varphi$ should be about 85°.

Two different Fourier syntheses of the electron density on the (0 0 1) plane, made with the signs of the structure factors which may be calculated for the two $\varphi$ values, are in agreement with the conclusions deduced from the behaviour of the structure factors, since only one of these two gave a definite image of the molecules (Fig. 5), in good accordance with possible models. It was then possible to determine, in a more precise way, the position of the molecule which is at $\varphi = 56°$. Moreover, the Fourier projection enabled us to refine the model of the molecule in such a way that its projection, perpendicular to

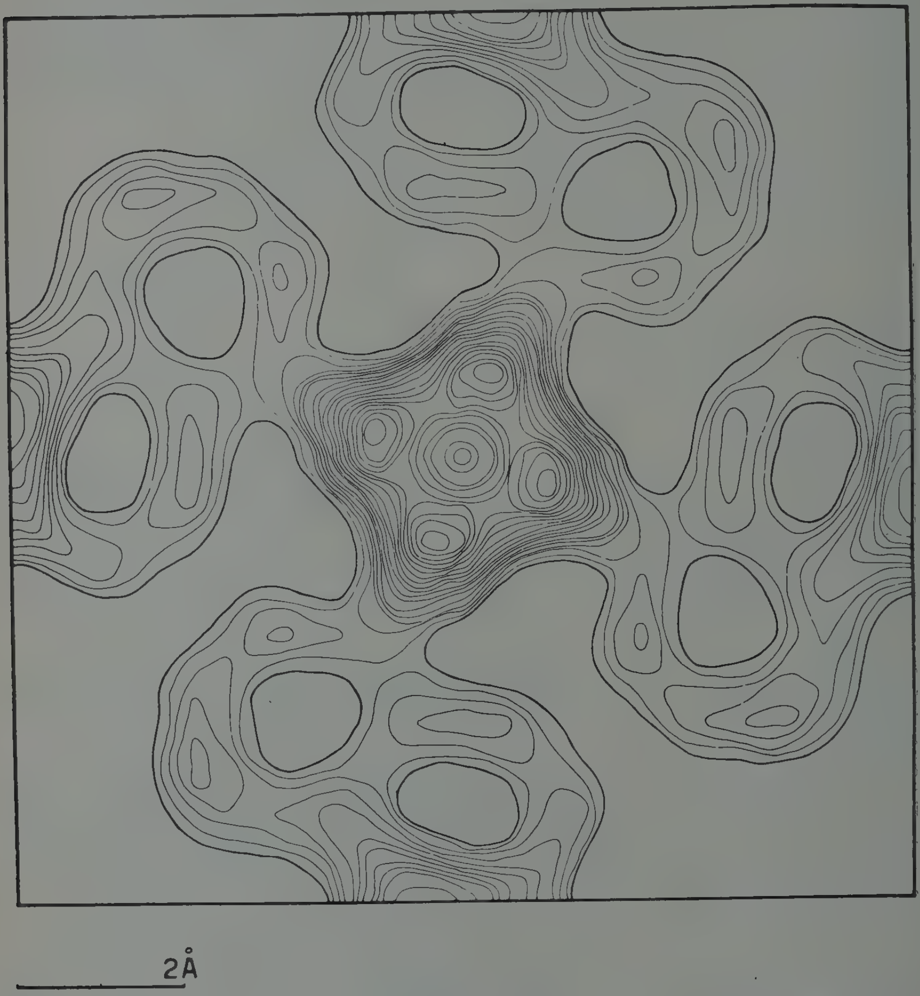

Fig. 5. – Fourier projection of the electron density on the (0 0 1) plane (levels in arbitrary units).

the chain axis, better corresponds to the experimental Fourier image. The model, drawn in Fig. 1, that we reached, does not much deviate from that first postulated.

TABLE III. – *Comparison between observed and calculated structure factors of poly-alpha-vinylnaphtalene.*

The $F_{o.}$ values correspond to the square root of the total intensity diffracted by the general $(hkl)$ lattice plane after effecting the usual corrections for the angular factors. In order to take into account the different multiplicity of the reflections, the $(hh0)$ and $(h00)$ calculated structure factors were divided by $\sqrt{2}$.

| $h\,k\,0$ | $F_{c.}$ | $F_{o.}$ | $h\,k\,0$ | $F_{c.}$ | $F_{o.}$ | $h\,k\,1$ | $F_{c.}$ | $F_{o.}$ |
|---|---|---|---|---|---|---|---|---|
| 2 0 0 | 264 | 263 | 9 1 0 | 33 | 74 | 2 1 1 | 358 | 308 |
| 2 2 0 | 150 | 67 | 9 3 0 | 64 | 90 | 3 2 1 | 220 | 282 |
| 3 1 0 | 144 | 118 | 10 0 0 | 92 | 83 | 4 1 1 | 368 | 387 |
| 4 0 0 | 60 | 61 | 8 6 0 | | | 4 3 1 | 172 | 171 |
| 4 2 0 | 88 | 172 | 10 2 0 | 41 | — | 5 2 1 | 67 | 124 |
| 5 1 0 | 8 | — | 9 5 0 | 24 | — | 6 1 1 | 86 | 129 |
| 4 4 0 | 130 | 127 | 10 4 0 | 87 | 125 | 5 4 1 | 3 | — |
| 5 3 0 | 7 | — | 11 1 0 | 47 | — | 6 3 1 | 137 | 169 |
| 6 0 0 | 69 | 97 | 8 8 0 | 2 | — | 7 2 1 | 36 | 91 |
| 6 2 0 | 27 | — | 11 3 0 | 25 | — | 6 5 1 | 122 | 85 |
| 7 1 0 | 4 | — | 9 7 0 | | | 8 1 1 | 140 | 113 |
| 6 4 0 | 21 | — | 10 6 0 | 119 | 117 | 7 4 1 | | |
| 7 3 0 | 81 | 98 | 12 0 0 | 41 | — | 8 3 1 | 54 | 85 |
| 8 0 0 | 4 | — | 11 5 0 | 46 | 78 | 9 2 1 | 144 | 88 |
| 8 2 0 | 63 | 59 | 12 2 0 | 10 | — | 7 6 1 | | |
| 6 6 0 | 23 | — | 12 4 0 | 11 | — | 8 5 1 | 102 | 89 |
| 7 5 0 | 68 | 66 | 10 8 0 | 26 | 70 | 9 4 1 | 94 | 93 |
| 8 4 0 | 38 | — | | | | 10 1 1 | 73 | — |

It was thus confirmed that the naphtalene plane does not bisect the $C_1\widehat{C_2}C_1'$ angle exactly, but is inclined by 68° in respect of the $C_1C_2C_3$ plane, whereas the $C_1\widehat{C_2}C_3$, $C_1\widehat{C_2}C_1'$, $C_1'\widehat{C_2}C_3$ angles result in good approximation tetrahedral. An analogous phenomenon was observed for poly-ortho-methylstyrene.

The calculation of the structure factors performed for the model found and oriented in the unit cell, as illustrated above, gave a satisfactory accordance between the observed and calculated structure factors (see Table III), and substantially confirmed the proposed structure (Fig. 6).

Also for poly-alpha-vinylnaphtalene, as for poly-ortho-methylstyrene [2] we did not find it advisable to make corrections for the thermal factor, owing to the low values of $2\sin\vartheta$ involved.

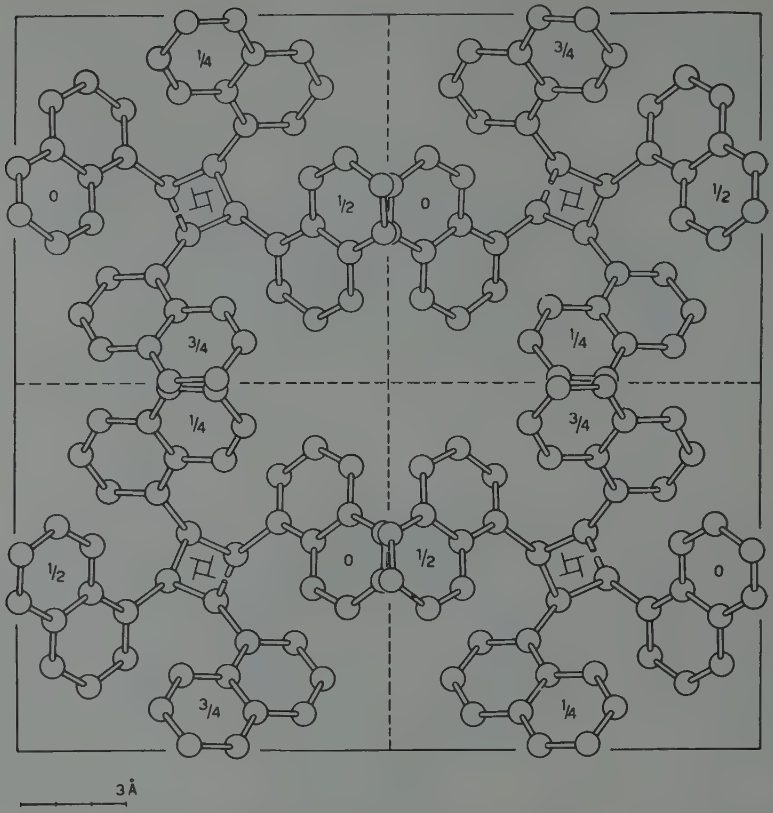

Fig. 6. – Model of the structure of poly-alpha-vinylnaphtalene projected on (001).

For a discussion of the structure of poly-alpha-vinylnaphtalene, we refer to our paper of this series on poly-ortho-methylstyrene which possesses an analogous chain form and mode of packing of the macromolecules.

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SUPPLEMENTO AL VOLUME XV, SERIE X
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# The Crystal Structure of cis 1,4 Polybutadiene.

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(ricevuto il 26 Giugno 1959)

In previous works [1], we announced the identification and discussed the structure of three of the four possible pure stereoisomers of polybutadiene; two with 1,2 enchainment (isotactic and syndiotactic respectively) and the third with trans 1,4 enchainment.

In a letter to the Editor of *Angewandte Chemie* we have given preliminary data concerning the crystal structure of the polymer with cis 1,4 configuration, of which we succeeded in preparing sufficiently long and crystallizable macromolecular chains formed by cis 1,4 units [2].

All the various stereoisomeric polymers we examined, were prepared with different catalysts, all obtained by reaction of metalalkyls on suitable compounds of transition elements [3].

For all these catalysts the mechanism of the polymerization reaction is of the co-ordinated anionic type; the different behavior can be ascribed to the mode of co-ordination of the olefin with the metallorganic complex of the transition metal.

As it is well known, polybutadienes, previously prepared by methods of the radicalic or cationic polymerization type, had always given amorphous products and when examined by infrared methods showed the presence of monomeric units having 1,2 enchainment together with monomeric units having 1,4 enchainment and cis and trans 1,4 configurations, irregularly distributed along the polymeric chain. At first the preparation of polybutadiene having very high cis 1,4 content was realized fractionating a mixture of macromolecules with 1,4 enchainment and different steric composition [4]. Following this method it was possible to obtain fractions having a melting point almost of 0 °C, consisting of macromolecules showing a cis 1,4 configuration for very long sections of their chains, at least. In fact, the melting point of these fractions is practically the same as that observed in polymers successively prepared with other highly stereospecific catalysts, which give crude products having a content in cis 1,4 units greater than 98%, The melting point of practically pure (> 99% of cis 1,4 units), unstretched, polybutadienes prepared in this Institute is +1°C [5].

In this note we will only report the data which we have obtained on the structure of cis 1,4 polybutadiene, which differs from the other pure stereoisomeric butadiene polymers for a greater similarity with natural, rubber due to its properties of possessing highly reversible elasticity with low hysteresis and of crystallizing under stretch at room temperature and even at higher temperatures.

In Table I, to make an example, we give some mechanical properties measured for a sample of our polymer, which are very similar to those obtainable for natural rubber.

TABLE I. – *Physical properties of vulcanized polybutadienes with a high content in cis 1,4 stereoisomer (pure gum recipe).*

| cis 1-4 content | 92 – 93% | 98 – 99% |
|---|---|---|
| Mooney viscosity ML 4 | 90 – 95 | 70 – 80 |
| Tensile stress (psi) | 800 – 1 100 | 2 500 – 2 800 |
| Elongation at break % | 900 – 1 000 | 850 – 950 |
| Modulus at 300% elongation (psi) | 140 – 180 | 140 – 180 |
| Resilience at 20 °C % | 80 – 85 | 85 – 88 |
| Hardness, Shore A | 45 – 50 | 45 – 50 |

Compounding recipe:

| | |
|---|---|
| Polybutadiene | 100 |
| Stearic acid | 2 |
| Zinc oxide | 3 |
| Sulphur | 1 |
| Vulcafor MBTS (di-2-benzothiazyl disulphide) | 1,3 |
| Nonox D (phenyl-β-naphtylamine) | 1 |

Cure: 145 °C × 45 min.

## 1. – Roentgenographic data.

The cis 1,4 polybutadiene has a melting point of about +1 °C; but as it was above quoted, it may exist in the crystalline state under stretching also at room temperature and even at higher temperatures.

The X-ray spectra of the polymer have been effected by us in a cylindrical camera for samples stretched at $(300 \div 400)\%$ and cooled at about $-30$ °C with a jet of carbon dioxide from dry ice, in order to have reflections as sharp as possible.

The examined samples supply fiber photographs very rich in reflections which denote a high order degree both for equatorial and longitudinal directions (Fig. 1).

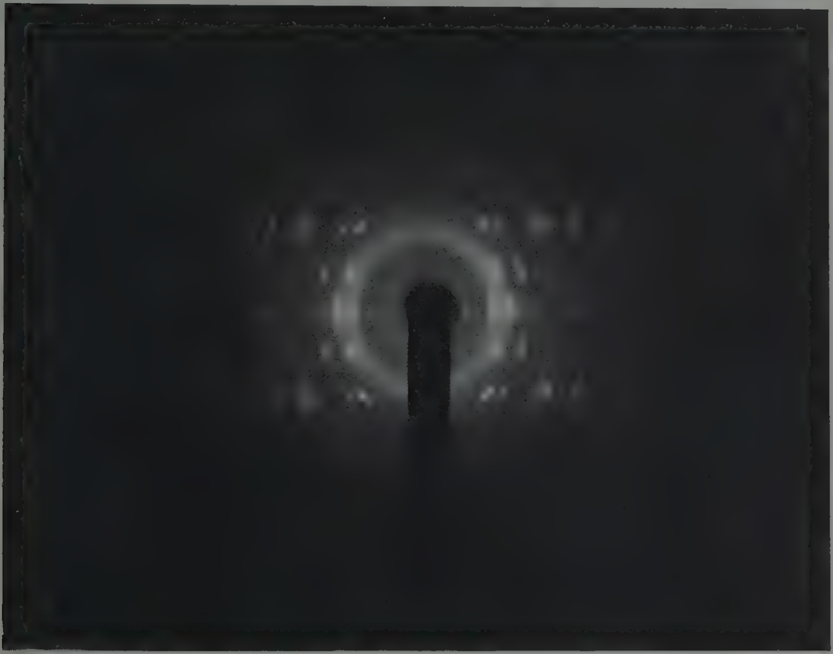

Fig. 1. – Fiber spectrum of cis 1,4 polybutadiene.

The establishment of the unit cell was effected by the standard methods of the reciprocal lattice [6].

The unit cell appeared monoclinic; its constants are $a = 4.60$ Å, $b = 9.50$ Å, $c = 8.60$ Å (fiber axis). The axis $c$ is inclined on the axis $a$; the angle between the axes results $\beta = 109°$ (all data within about 1% accuracy).

The calculated density, assuming that in the unit cell 4 monomeric units are contained, is 1.01, in accordance with the experimental value.

The most characteristic extinction, which becomes evident from the reciprocal lattice description is that of $hkl$ reflections with $h+k = 2n+1$. This extinction is common to 5 monoclinic space groups say $C_s^3$, $C_s^4$, $C_2^3$, $C_{2h}^3$, $C_{2h}^6$ [7].

Some of these space groups are characterized by further extinctions, as reported below:

$C_s^3$ none; $C_s^4$ $h0l$ if $l = 2n+1$; $C_2^3$ none

$C_{2h}^3$ none; $C_{2h}^6$ $h0l$ if $l = 2n+1$

Actually, it was not possible to observe any reflection $h0l$ with $l = 2n+1$: then we found it advisable to retain $C_s^4$ and $C_{2h}^6$ as the most probable space groups.

As well known, the univocous establishment of the space group of the unit cell of a polymer must be generally delayed, until reasonable considerations relative to the symmetry of the macromolecules and to their mode of packing may be made. Two different conformations are possible for the monomeric unit on the basis of the principle of staggered simple bonds [8] we have already discussed in previous works. They are schematically illustrated in Fig. 2, where we have shown for each of them two projections, normal to the chain axis.

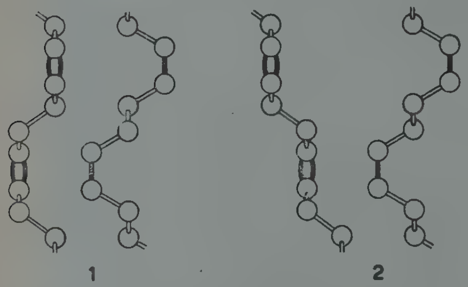

Fig. 2. – Possible conformations of a succession of 1,4 cis polybutadiene monomeric units satisfying the principle of staggered bonds.

In natural rubber, the conformation 2 is actually present in the crystalline state [9].

In our case the period calculated for the conformation 2 with normal distances and angles (8.4 Å) is in much better agreement with the period we found experimentally (8.6 Å) than with the period calculated for the conformation 1 (8.1 Å).

In the type 2 conformation the arrangement of the monomeric units gives rise to a glide plane type chain, which satisfies the principles of staggered bonds and the minimum energy postulate [8]. The chain contains symmetry centers and, as said above, a glide plane with translation. These symmetry elements are contained all together in the space group $C_{2h}^6$. These considerations brought us to effect the study of the structure models corresponding to this space group and to compare the experimental and calculated intensities, in order to reach a confirmation of the space group. On the basis of this assumption since two chains in 000 and $\frac{1}{2}\frac{1}{2}0$ must be contained in the cell, the positions of only two carbon atoms are enough for describing the whole structure.

A very good agreement between experimental and calculated intensities (Table III) was obtained assuming the co-ordinates given in Table II.

TABLE II. – *Co-ordinates of the independent structural units of polybutadiene.*

| | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| $CH_2$ | 0.112 | 0.000 | 0.088 |
| CH | 0.046 | 0.127 | 0.183 |

TABLE III. – *Comparison between the observed and calculated structure factors* ($B = 5.7$ Å$^2$).

| $h\ k\ l$ | $F_{c.}$ | $F_{o.}$ | $h\ k\ l$ | $F_{c.}$ | $F_{o.}$ |
|---|---|---|---|---|---|
| 0 2 0 | 32 | 37 | 2 4 1 | < 1 | — |
| 1 1 0 | 42 | 45 | $3\ 1\ \bar{1}$ | 2 | — |
| 1 3 0 | 1 | — | $3\ 3\ \bar{1}$ | 1 | — |
| 0 4 0 | — | — | 3 1 1 | 4 | — |
| 2 0 0 | 15 | 16 | $2\ 6\ \bar{1}$ | 5 | 7 |
| 2 2 0 | 2 | — | $1\ 7\ \bar{1}$ | | |
| 1 5 0 | 1 | — | $1\ 1\ \bar{2}$ | 16 | 21 |
| 2 4 0 | 6 | — | 0 2 2 | 11 | 13 |
| 0 6 0 | 10 | 12 | 1 1 2 | 16 | 18 |
| 3 1 0 | < 1 | — | $1\ 3\ \bar{2}$ | 21 | 23 |
| 3 3 0 | 6 | — | $2\ 0\ \bar{2}$ | 12 | 12 |
| 1 7 0 | 9 | 9 | $2\ 2\ \bar{2}$ | 25 | 19 |
| 2 6 0 | 1 | — | 0 4 2 | | |
| 0 8 0 | 10 | 12 | 1 3 2 | | |
| 3 5 0 | 4 | — | 2 0 2 | 19 | 18 |
| $1\ 1\ \bar{1}$ | 32 | 35 | $1\ 5\ \bar{2}$ | 12 | 13 |
| 0 2 1 | | | $2\ 4\ \bar{2}$ | 13 | 10 |
| 1 1 1 | 17 | 21 | 2 2 2 | | |
| $1\ 3\ \bar{1}$ | 10 | 8 | 1 5 2 | 3 | — |
| 1 3 1 | 11 | 10 | $3\ 1\ \bar{2}$ | 5 | — |
| 0 4 1 | 1 | — | 0 6 2 | 3 | — |
| $2\ 2\ \bar{1}$ | 8 | 8 | 2 4 2 | 1 | — |
| 2 2 1 | 11 | 10 | $3\ 3\ \bar{2}$ | 3 | — |
| $1\ 5\ \bar{1}$ | 6 | 7 | $2\ 6\ \bar{2}$ | 6 | — |
| 1 5 1 | 7 | 7 | $1\ 7\ \bar{2}$ | 4 | — |
| $2\ 4\ \bar{1}$ | < 1 | — | 3 1 2 | 10 | 9 |
| 0 6 1 | 8 | 9 | 0 0 2 | 6 | 6 |

In Fig. 3 the resulting mode of packing is shown.

As it may be seen, it is particularly simple and allows a homogeneous filling of the space. The contact distances between carbon atoms of neighbouring molecules are all greater than 3.8 Å, in good accordance with the results obtained examining other known structures. The Fourier projection of the electron density on (001) is shown in Fig. 4.

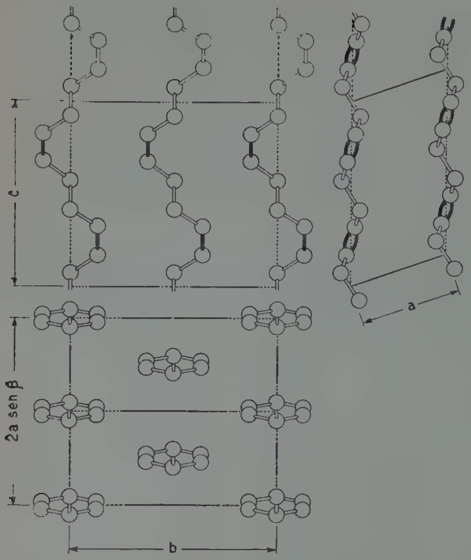

Fig. 3. – Model of the structure of cis 1,4 polybutadiene.

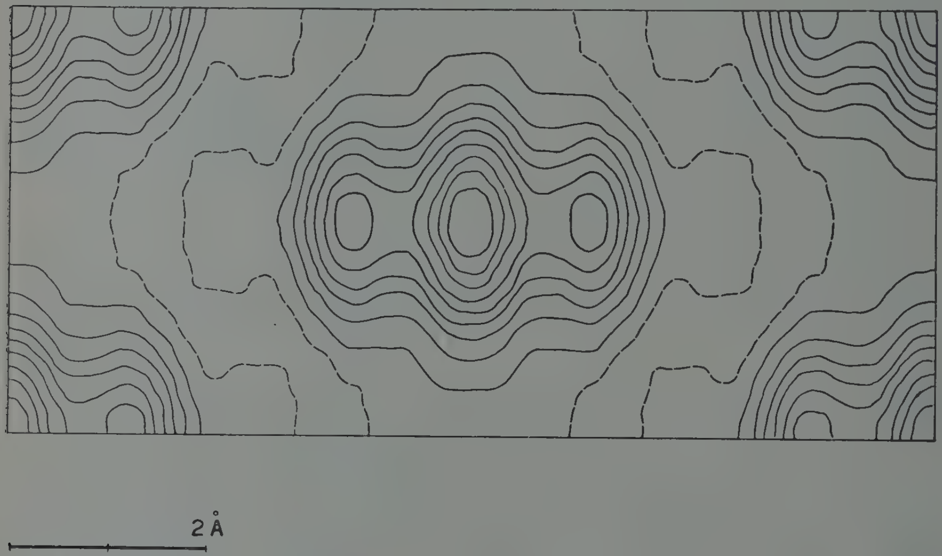

Fig. 4. – Projection of the electron density on (001) (contours are drawn at 1$e$/Å$^2$, the dashed line represents the 1$e$/Å$^2$ level).

## 2. – Comparison of the chain structures of the different stereoisomeric polybutadienes.

By the synthesis of cis 1,4 polybutadiene and the determination of its structure the study of the series of the pure stereoisomers of polybutadiene was completed; we think it is interesting, therefore, to compare the different structures we found. The case of 1,2 polymerization is analogous to the one of vinyl polymers; the two only possibilities of forming a crystallizable polymer having a regular and simple structure, are those of having an isotactic polymer (for which a threefold screw chain conformation was expected and has been actually found) or a syndiotactic polymer (for which the structural equivalence of the monomeric units is realized by the presence of a glide plane with translation along the fiber axis [1]).

Whereas the polymerization occurs with the formation of chains having 1,4 enchainment, one of the two possible pure stereoisomers (which have also been studied by us) is with regular cis 1,4 enchainment, and the other with regular trans 1,4 enchainment. It is interesting to note how, in their pure state, both polymers having 1,2 enchainment and the one having trans 1,4 enchainment do not show elastomeric characteristics at room temperature, but, on the contrary, they show features of crystalline products, able to be oriented by mechanical treatments and, therefore, to form fibers. These features which were not foreseen for a polymer of butadiene, may be easily understood because of the high cristallinity at room temperature, the high molecular weight and the high melting temperature.

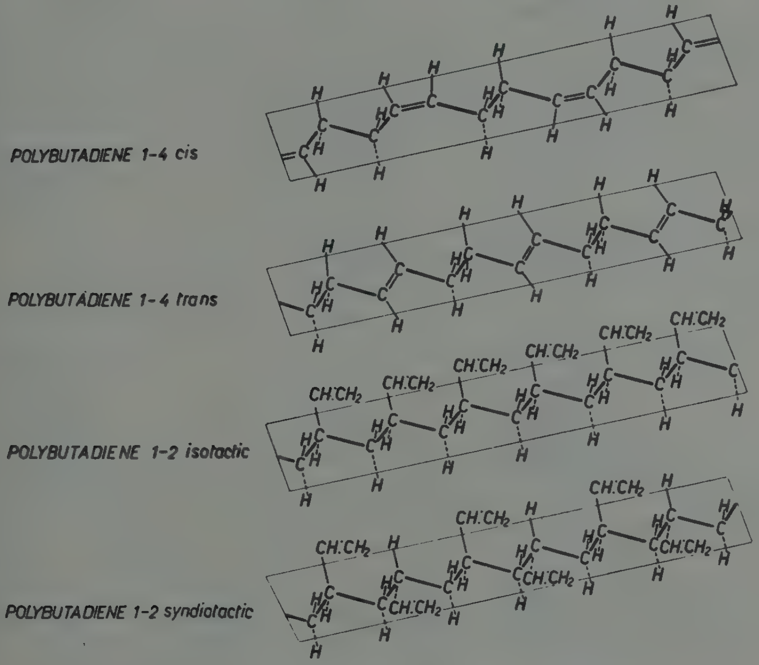

Fig. 5. - Configurations of the four possible regular chains of polybutadiene.

In Fig. 5 and 6, we have shown the models of the chains of the 4 stereoisomeric polymers of butadiene whose main chains are arbitrarily stretched on a plane (Fig. 5) and the conformations they actually assume in the crystalline state (Fig. 6). All the observed conformations satisfy the principle of the staggered simple bonds, also for the carbon atoms adjacent to the double bond.

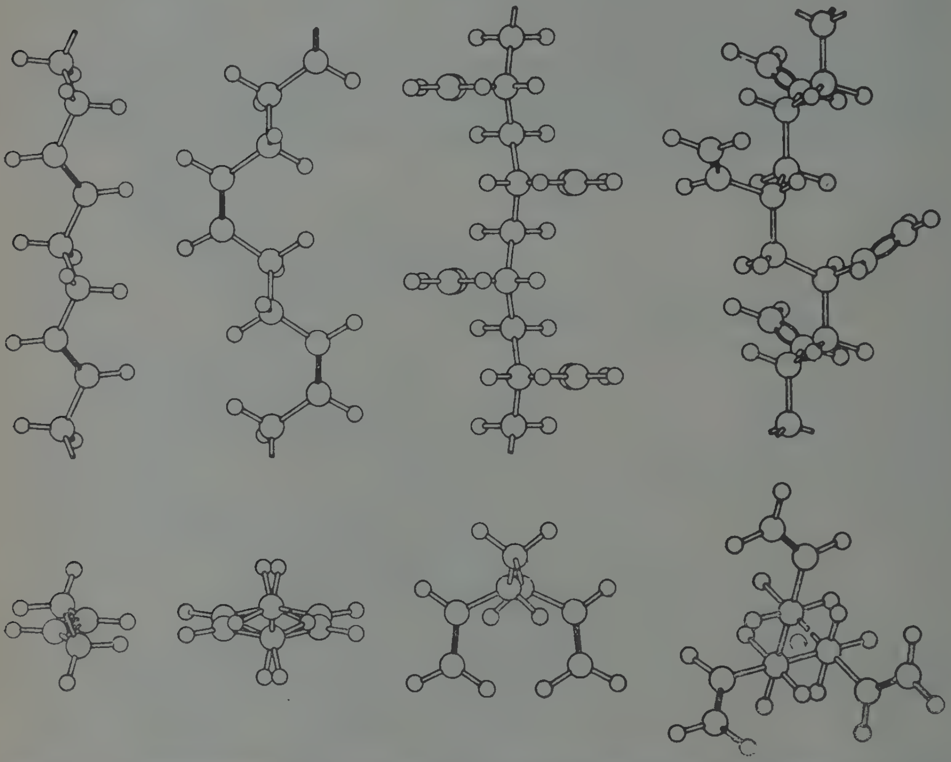

Fig. 6. - Conformations in the crystalline state of the four possible regular chains of four known polybutadiene (trans, cis 1-4 syndio-, isotactic 1-2).

The packing of the chains occurs for 1,2 syndiotactic polybutadiene and for cis 1,4 polybutadiene, whose chains contain glide planes with translation along the fiber axis, by a regular juxtaposition of the chains on these planes. These planes pack themselves one near another so that each chain has the highest number of neighbouring chains structurally equivalent among themselves.

For the trans 1,4 polybutadiene, the almost filiform chains are packed together in a pseudo-hexagonal lattice, whilst for the isotactic 1,2 polybutadiene, the packing is rhombohedral because of the presence of crystallographic screw axes, $3_1$ and $3_2$, in the lattice.

## 3. - Comparison of the structure of cis 1,4 polybutadiene with that of cis 1,4 polyisoprene.

It is also interesting to compare the structure we have found for cis 1,4 polybutadiene with that of cis 1,4 polyisoprene in the crystalline state (natural rubber).

The crystalline structure of natural rubber has been studied several times by many Authors; but now it appears definitely resolved owing, above all, to the works performed by Bunn [10] and Nyburg [9]. Natural rubber, according to the latter, has a monoclinic unit cell, with axes at 90°, space group $P2_1/a$.

However, after examining the co-ordinates of the ten atoms of two monomeric units describing the independent structural unit $(x, y, z)$ according to Nyburg, it may be easily noted that they are not independent one of another; the independent unit is actually formed by only one monomeric unit in $x, y, z$ which along the chain is followed by another one in $\frac{1}{2}-x,\ y,\ \frac{1}{2}+z$. Under this condition (implicit in the Nyburg co-ordinates) the space group must be chosen as *Pbac*, which adds to the four general positions of $P2_1/a$ the other 4 obtainable by effecting the transformation $(\frac{1}{2}-x,\ y,\ \frac{1}{2}+z)$ on themselves. Also, according to Nyburg, molecules described by $x$, $y$, $z$ co-ordinates, may be statistically replaced by the corresponding molecules having co-ordinates $(x,\ \frac{1}{8}-y,\ z)$. Only by this assumption it has been possible to obtain a good agreement between experimental and calculated intensities.

Nevertheless, the hypothesis of a completely random vicariance in the same crystal site of mirrored macromolecules in respect of the plane $y=\frac{1}{8}$ does give rise to some unsuitable Van der Waals contacts ($< 3.2$ Å) between carbon atoms of different chains.

The difficulties are less if, instead of an isomorphous statistical substitution of the single chain, we consider an isomorphous statistical substitution of two different types of layers of monomolecular thickness.

Let us consider (Fig. 7) the succession of molecules ABA, that can be described by the space group *Pbac* on the projection on *ab* and *ac*. All the carbon atoms of the molecules are interested in intermolecular contacts and these contacts do not overcome those we have found for cis 1,4 polybutadiene.

A layer of molecules CDC ... packs, according to the space group *Pbac*, with the layer ABA. The contacts between C and D are analogous to those between A and B.

The contact of the molecule C with the molecules A and B is effected, on the contrary, only by the methyl group.

But then analogous contacts may be effected by a C′D′ layer, mirrored in respect to the CD layer in the plane $y = \frac{1}{8}$. We think, therefore, that there is evidence to believe that an ABAB layer may pack at pleasure with a CD or a C′D′ layer. The total effect on the intensities is as if a mirror in $y = \frac{1}{8}$ actually existed; but the contacts between C and D′ (of about 3.1 Å),

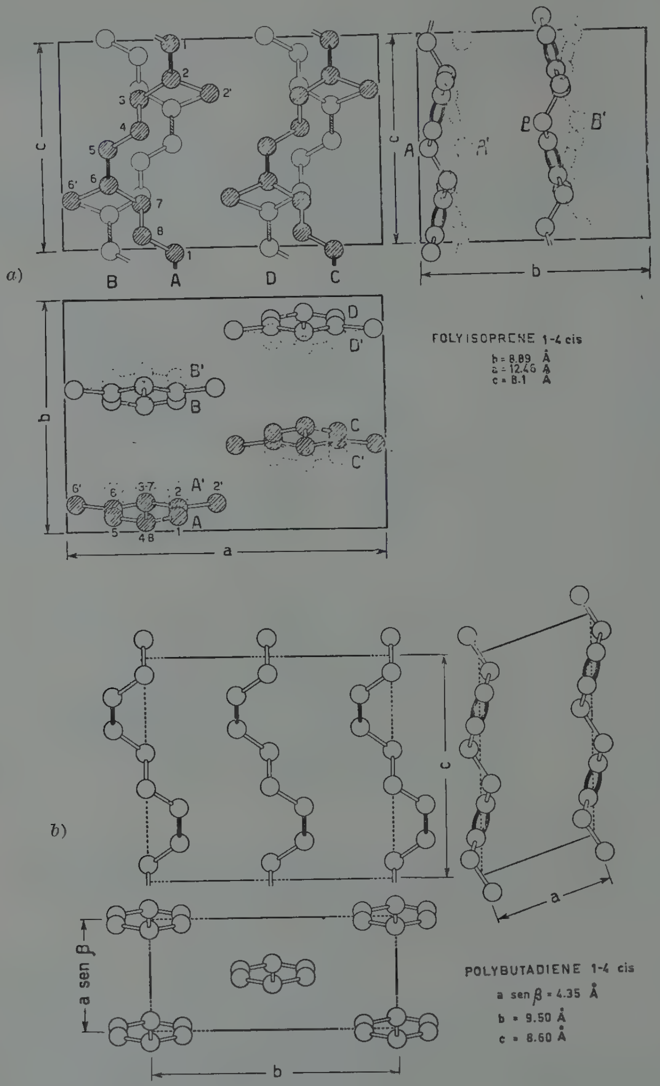

Fig. 7. – Comparison between the crystal structures of cis 1,4 polyisoprene and that of cis 1,4 polybutadiene.

implied by the Nyburg model, who assumes the possibility of having an irregular succession CDC′D... does not occur any more.

Thus, the analogy with cis 1,4 polybutadiene is more complete. In both cases the molecules follow one another almost at the same distance, along the symmetry plane with translation.

The presence of methyl groups leads, in the cis 1,4 polyisoprene, to an increase of the unit cell size in the direction normal to the symmetry plane with translation $c(a_{PI} > b_{PB})$ to the fact that $b_{PI}$ is about the double of $a \sin \beta_{PB}$ because along the glide plane a succession of anticlined molecules must be represented.

We can finally observe that in all polymers whose chains contain a symmetry plane with translation (polyvinylchloride, syndiotactic 1,2 polybutadiene, cis 1,4 polybutadiene, cis 1,4 polyisoprene, this symmetry element is kept in the crystalline state and determines the space packing of the macromolecules among themselves.

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SUPPLEMENTO AL VOLUME XV, SERIE X
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# Spettri infrarossi di polimeri stereoordinati di monomeri vinilaromatici.

## 1. - Polistirolo isotattico.

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La struttura cristallina di alcuni polimeri isotattici ottenuti con processi di polimerizzazione stereospecifica è stata oggetto di vari lavori che hanno portato alla conclusione che l'ordinamento isotattico comporta in generale una configurazione elicoidale delle macromolecole ordinate nel reticolo cristallino[1].

Nella serie di note di cui iniziamo la pubblicazione trattando il caso del polistirolo isotattico esporremo i risultati ottenuti dall'esame spettrografico infrarosso di polimeri stereoordinati di monomeri vinilaromatici e dei corrispondenti polimeri preparati con metodi convenzionali non stereospecifici. Il confronto fra prodotti delle due classi ci ha permesso di mettere in evidenza significative differenze che chiariscono alcune relazioni fra struttura stereoordinata ed assorbimento infrarosso.

### 1. – Parte sperimentale.

1·1. *Apparecchiatura usata*. Per la registrazione degli spettri infrarossi presentati in questo studio abbiamo impiegato uno spettrofotometro a doppio raggio Perkin-Elmer Mod. 21 con ottica di cloruro sodico. I campioni sono stati esaminati sotto forma di lamine sottili montate su supporti di tipo comune. Le osservazioni in luce polarizzata sono state effettuate usando polarizzatori a trasmissione con lamine di cloruro d'argento e celle rotanti dei tipi comunemente forniti dalla Perkin-Elmer.

1·2. *Preparazione dei campioni*. Il campione di polistirolo isotattico da noi usato per la preparazione delle lamine studiate proveniva da una prova di polimerizzazione stereospecifica dello stirolo in presenza di un catalizzatore ottenuto per reazione fra tetracloruro di titanio e alluminio trietile nelle condizioni descritte nel lavoro di DANUSSO e SIANESI [2]. Dal prodotto della reazione di polimerizzazione è stata isolata la frazione insolubile in metiletilchetone avente una viscosità intrinseca di 2.8 in tetralina a 100 °C ed un punto di fusione roentgenografico di (238 ÷ 240) °C. La percentuale di cristallinità, determinata sempre per via roentgenografica per confronto fra le aree di diffrazione della parte amorfa e della parte cristallina su campioni sottoposti a ricottura per qualche ora a 150 °C, è risultata del 40 % circa.

Le pellicole di polistirolo isotattico esaminate all'infrarosso sono state ottenute per stampaggio fra piastre metalliche riscaldate alla temperatura di 250 °C limitando il più possibile la durata dell'operazione per evitare alterazioni del prodotto. Lo spessore dei film utilizzati per la registrazione degli spettri è stato dell'ordine di (0,05 ÷ 0.07) mm. Raffreddando bruscamente i film ottenuti per stampaggio abbiamo preparato campioni di polistirolo isotattico allo stato amorfo, mentre riscaldando i campioni amorfi a temperature comprese fra quella di transizione vetrosa e quella di fusione si è verificata una parziale cristallizzazione del prodotto.

Il polistirolo atattico usato per il confronto spettrografico era un comune polistirolo commerciale ottenuto allo stato di film di spessore conveniente per stampaggio alla temperatura di 130 °C.

I campioni orientati necessari per l'esame in luce polarizzata sono stati ottenuti procedendo allo stiramento di un film di polimero amorfo ad una temperatura poco superiore a quella di transizione vetrosa. Regolando opportunamente la temperatura e la tensione alla quale il campione era sottoposto abbiamo preparato film con un grado d'orientamento notevole come quello che ha fornito gli spettri riportati nella Fig. 5. Durante il processo di stiramento di campioni isotattici amorfi abbiamo potuto ottenere campioni cristallini orientati o campioni non cristallini parzialmente orientati in funzione della temperatura, della durata dell'operazione e della tensione esercitata.

## 1·3. *Risultati ottenuti.*

*a*) Spettro del polistirolo isotattico. – La Fig. 1 riporta gli spettri del polistirolo isotattico nella regione fra 2 e 15 μm per il prodotto allo stato amorfo (campione ottenuto per brusco raffreddamento di un film portato alla fusione) e allo stato cristallino (dopo ricottura dello stesso campione a 180 °C). Le numerose bande che compaiono soltanto nello spettro del prodotto cristallino non sono dovute ad alterazione chimica del campione, ma al passaggio di stato amorfo-cristallino come conseguenza di un fenomeno di cristallizzazione nel senso che definiremo meglio in seguito. Queste bande infatti scompaiono rifondendo il campione e riottenendolo allo stato amorfo.

Le differenze più evidenti fra i due spettri del polistirolo isotattico amorfo e cristallino compaiono nella regione a frequenze inferiori a 1400 cm$^{-1}$: le bande interessate sono contrassegnate nella Tab. I con un asterisco che distingue gli assorbimenti caratteristici del prodotto cristallino.

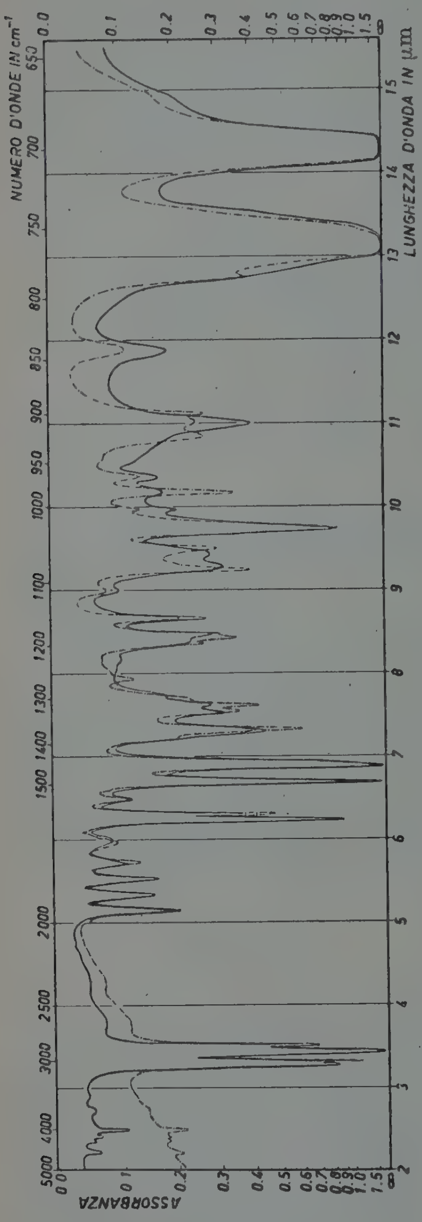

Fig. 1. – Spettri infrarossi di un polistirolo isotattico: —— amorfo; -·-·-· cristallino.

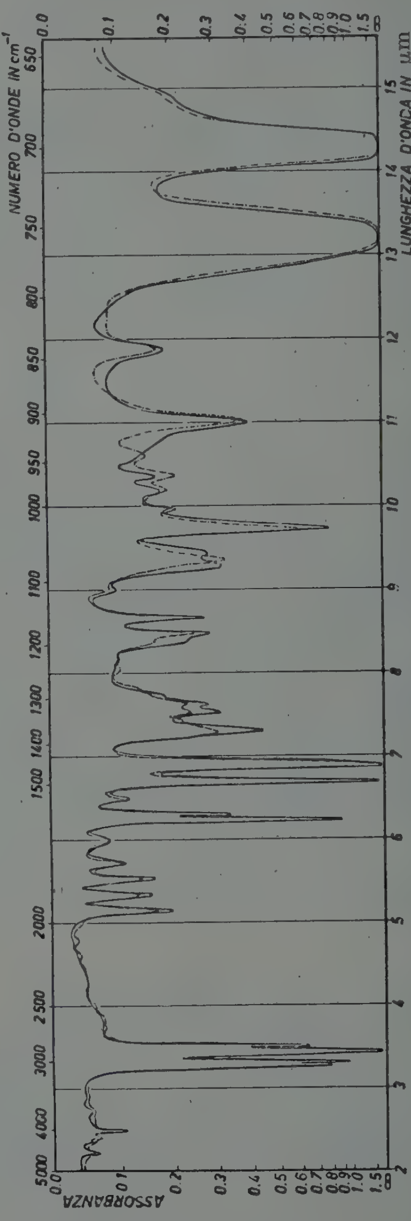

Fig. 2. – Spettri infrarossi di un polistirolo: —— isotattico amorfo; -·-·-· atattico.

Tabella I. – *Spettro infrarosso del polistirolo.*

| Isotattico amorfo | | Isotattico cristallino | | | |
|---|---|---|---|---|---|
| Frequenza | Intensità | Frequenza | Intensità | Polarizzazione | Specie di simmetria |
| 670 | fl | 670 | fl | π | — |
| 700 | mf | 700 | mf | π | — |
| 751 | fl | 751 | fl | σ | — |
| 760 | mf | 760 | mf | π | — |
| — | — | (*) 784 | d | π | *A* |
| 842 | d | 842 | d | — | — |
| — | — | (*) 897 | m | π | *A* |
| 907 | m | 907 | m | — | — |
| — | — | (*) 920 | m | π | *E* |
| 945 | fl | 945 | fl | — | — |
| 965 | md | 965 | md | σ | — |
| 983 | d | 983 [981 (*)<br>984 (*)] | m | π<br>σ | *A*<br>*E* |
| 1002 | md | 1002 | md | — | — |
| 1026 | f | 1026 | f | σ | — |
| 1061 | m | (*) 1052 | m | σ | *E* |
| 1078 | m | (*) 1083 | m | σ | *E* |
| 1110 | md | 1110 | md | σ | — |
| 1156 | m | 1156 | m | — | — |
| 1179 | m | 1179 | fl | σ | — |
| — | — | (*) 1189 | m | π | *A* |
| 1195 | fl | (*) 1195 | d | π | — |
| 1240 | fl | 1240 | fl | σ | — |
| — | — | (*) 1260 | md | σ | *E* |
| 1298 | fl | 1298 | d | π | — |
| — | — | (*) 1302 | d | π | *A* |
| 1314 | m | 1314 | m | σ | — |
| 1326 | m | 1326 | m | σ | — |
| 1365 | m | 1365 | m | σ | — |
| 1387 | fl | 1387 | fl | σ | — |
| 1440 | fl | 1440 | fl | σ | — |
| 1451 | f | 1451 | f | σ | — |
| 1490 | f | 1490 | f | σ | — |
| 1541 | d | 1541 | d | σ | — |
| 1582 | m | 1582 | m | σ | — |
| 1600 | f | 1600 | f | σ | — |
| 1664 | md | 1664 | md | — | — |
| 1742 | d | 1742 | d | σ | — |
| 1801 | d | 1801 | d | σ | — |
| 1871 | d | 1871 | d | σ | — |
| 1945 | m | 1945 | m | σ | — |
| — | — | (*) 1980 | fl | π | — |
| 2824 | fl | 2824 | fl | — | — |
| 2865 | m | 2865 | m | π | — |
| 2932 | mf | 2932 | mf | σ | — |
| 3030 | f | 3030 | f | σ | — |
| 3065 | m | 3065 | m | σ | — |
| 3083 | fl | 3083 | fl | — | — |

| | | | |
|---|---|---|---|
| mf molto forte | m media | md molto debole | π parallela |
| f forte | d debole | fl flesso | σ perpendicolare |

*b*) Confronto fra gli spettri del polistirolo isotattico e atattico. – Mentre sono assai sensibili, come si è visto, le differenze che il fenomeno della cristallizzazione fa intervenire nello spettro del polistirolo isotattico, quasi nulle sono le differenze fra gli spettri del polistirolo isotattico amorfo e del polistirolo atattico. Si rileva infatti dalla Fig. 2, nella quale sono riportati gli spettri infrarossi dei due prodotti, che le differenze si riducono, nella regione fra 2 e 15 μm, ad uno sdoppiamento della banda a 1070 cm$^{-1}$ (Fig. 3) e all'attenuarsi della banda molto debole a 945 cm$^{-1}$ che si riduce ad un flesso sul fianco della banda di media intensità a 907 cm$^{-1}$ nel polistirolo isotattico amorfo. Inoltre la banda a 983 cm$^{-1}$ presente negli spettri di entrambi i campioni ha un'intensità leggermente superiore nel polistirolo isotattico amorfo, ma essa risulta molto influenzata dalla cristallinità del campione, come è dimostrato dalla Fig. 4.

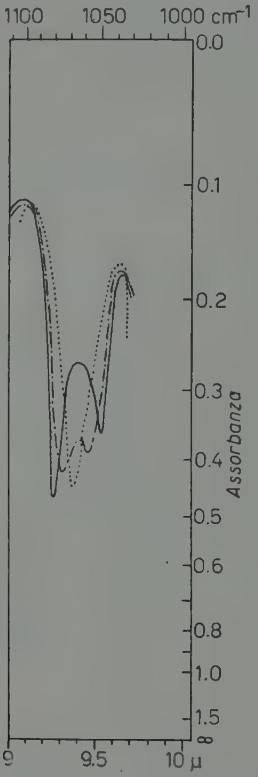

Fig. 3. – Regione a 1070 cm$^{-1}$ dello spettro infrarosso di un campione di polistirolo ····· atattico; -·-·-· isotattico amorfo; ——— isotattico cristallino.

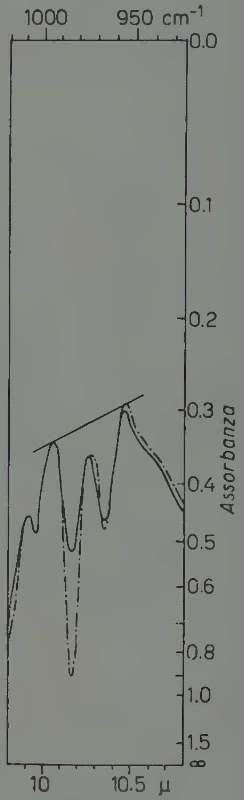

Fig. 4. – Regione a 980 cm$^{-1}$ dello spettro infrarosso di un campione di polistirolo isotattico ——— amorfo; -·-·-· cristallino.

*c*) Osservazione in luce polarizzata del polistirolo isotattico cristallino orientato. – La Fig. 5 riporta i risultati ottenuti dall'esame in luce polarizzata di un campione di polistirolo isotattico cristallino orientato secondo il procedimento descritto in precedenza. L'elevato rapporto dicroico di alcune bande di cristallinità ci permette di considerare buona l'orientazione della parte cristallina del campione esaminato, mentre poco si può dire circa la parte amorfa dello stesso campione. Vogliamo qui sottolineare come presentino spiccato dicroismo le bande segnalate in *b*) e come si verifichi per numerose bande lo sdoppiamento in bande a polarizzazione parallela e perpendicolare in accordo con la teoria discussa in seguito.

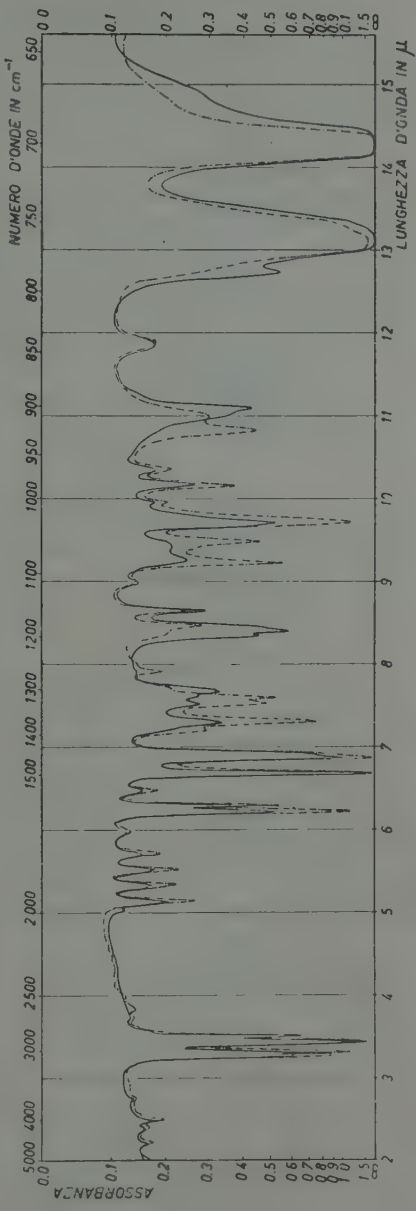

Fig. 5. Spettri infrarossi di un polistirolo isotattico cristallino orientato. Osservazione in luce polarizzata con il vettore elettrico: —— parallelo alla direzione di stiro; -·-·-· perpendicolare alla direzione di stiro.

## 2. – Previsione dello spettro del polistirolo isotattico.

Gli studi effettuati nel nostro Istituto con la diffrazione dei raggi X hanno permesso di stabilire che le catene nel polistirolo isotattico sono impacchettate in un reticolo appartenente al gruppo spaziale $R\,3c$ o $R\,\bar{3}c$ [3]. Considerata isolatamente, ogni catena possiede un periodo d'identità lungo l'asse di 6.65 Å corrispondente a tre unità monomeriche polimerizzate testa a coda con la stessa configurazione sterica dell'atomo di carbonio asimmetrico di ciascun gruppo —$CH(C_6H_5)$—$CH_2$— (Fig. 6).

Mentre nel polistirolo ottenuto con metodi di polimerizzazione convenzionali l'orientazione del gruppo fenilico è completamente casuale, nel polistirolo isotattico cristallino i piani dei nuclei benzenici posseggono tutti la stessa orientazione e sono sovrapponibili uno all'altro per effetto di una rotazione di un angolo di $\frac{2}{3}\pi$ seguita da una traslazione di un terzo del periodo di identità.

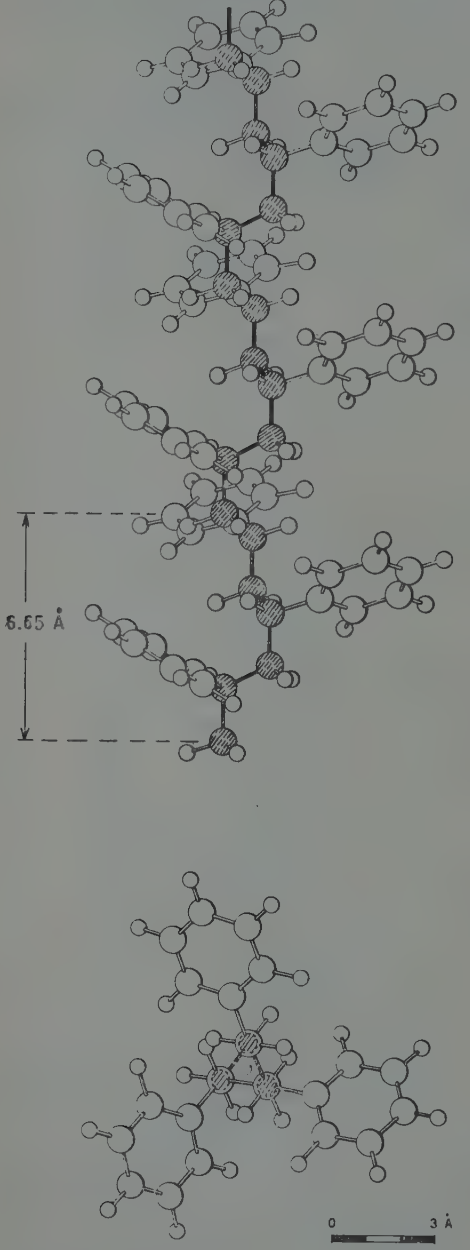

Fig. 6. – Configurazione di un tratto di catena di polistirolo isotattico cristallino.

L'isotassia e la cristallizzazione, introducendo queste perfette regolarità strutturali, creano la possibilità di interazioni fra le varie unità monomeriche della catena e fanno quindi cadere in larga parte i presupposti formulati in studi precedenti su macromolecole elicoidali [4] che supponevano un debole accoppiamento fra i modi di vibrazione delle singole unità. Ne consegue che lo spettro del polistirolo isotattico cristallino non può più essere considerato come derivante dalla semplice sovrapposizione dei modi normali approssimati dei gruppi $C_6H_5$—, $\rangle CH_2$ e $-\rangle CH$, in quanto la possibilità di accoppiamento di vibrazioni delle varie unità monomeriche entro il periodo d'identità può far comparire nuove bande d'assorbimento o alterare sensibilmente l'intensità di alcune delle presenti.

Il principio di trascurare possibili interazioni fra i moti delle diverse unità monomeriche è invece valido nei prodotti allo stato amorfo, anche per catene isotattiche, poichè la simmetria dell'elica viene distrutta come conseguenza del disordine creato da rotazioni statistiche intorno a tutti i legami semplici carbonio-carbonio. È pertanto giustificata in base a questa situazione la quasi perfetta identità degli spettri infrarossi del polistirolo isotattico amorfo e del polistirolo atattico.

Nella previsione dello spettro infrarosso del polistirolo isotattico si può considerare idealmente isolata dal reticolo una catena singola. Le approssimazioni che derivano da un'ipotesi di questo genere possono essere ritenute soddisfacenti per le due seguenti ragioni sperimentali rilevate nel corso dei nostri studi su polimeri con macromolecole elicoidali:

1) Le bande di cristallinità non scompaiono a seguito della formazione di soluzioni solide di polimeri a struttura cristallina analoga e quindi vicarianti. Questo primo punto è stato verificato cercando ad esempio di preparare per successive cofusioni soluzioni solide di polistirolo e di poliortofluorostirolo, polimeri che posseggono una struttura cristallina analoga dati i valori dei raggi equivalenti di fluoro e idrogeno.

2) Le bande di cristallinità scompaiono invece se si preparano copolimeri aventi una concentrazione di uno dei monomeri compresa fra il 30 e il 70%. Questa seconda affermazione è basata sulla constatazione sperimentale che copolimeri aventi nella stessa macromolecola unità monomeriche diverse (per esempio lo stirolo e il parametilstirolo), sottoposti ai trattamenti termici che nella parte sperimentale abbiamo definito di cristallizzazione, non presentano bande di cristallinità all'esame infrarosso, mentre alla diffrazione dei raggi X mostrano di possedere un reticolo cristallino sia pure diverso da quello degli omopolimeri corrispondenti.

Considerando una singola catena, l'unità sterica fondamentale, che si identifica con il periodo d'identità possiede, come unico elemento di simmetria, un'elicotrigira che definisce il gruppo di punti $C_3$ mediante il quale si può analizzare lo spettro infrarosso del polistirolo isotattico cristallino. Quest'analisi

TABELLA II. – *Numero, ripartizione, attività e polarizzazione dei modi normali per il gruppo di punti $C_3$.*

| $C_3$ | $E$ | $C_3^1(z)$ | $C_3^2(z)$ | $n_i$ | $T$ | $T'$ | $R'$ | $n'_i$ | Raman | Infrarosso | Polarizzazione |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $A$ | 1 | 1 | 1 | 48 | 1 | 8 | 9 | 30 | $a$ | $a$ | $\pi\ (T_z)$ |
| $E$ | 1 | $e^{2\pi i/3}$ | $e^{-2\pi i/3}$ | 48 | 1 | 8 | 9 | 30 | $a$ | $a$ | $\sigma(T_x, T_y)$ |
|  | 1 | $e^{-2\pi i/3}$ | $e^{2\pi i/3}$ | 48 | 1 | 8 | 9 | 30 | $a$ | $a$ |  |

| | |
|---|---|
| $n_i$ | vibrazioni normali complessive (interne + esterne + non genuine) |
| $T$ | traslazioni pure |
| $T'$ | vibrazioni esterne di tipo traslatorio |
| $R'$ | vibrazioni esterne di tipo rotatorio |
| $n'$ | vibrazioni interne |
| $a$ | attiva |
| $\pi$ | parallela |
| $\sigma$ | perpendicolare |

ci porta ad affermare che sono attive, in assorbimento infrarosso e nell'effetto Raman, solo quelle vibrazioni in cui si muovono in fase atomi in posizioni stericamente equivalenti di periodi d'identità diversi. I risultati della trattazione con la teoria dei gruppi dell'unità sterica fondamentale del polistirolo sono riportati nella Tabella II.

È opportuno ricordare qui che per il gruppo di punti $C_3$ nessuna banda viene vietata dalle regole di selezione e che, nell'ipotesi che tutte le vibrazioni delle diverse unità monomeriche interagiscano fortemente fra loro, ogni banda presente nello spettro del polistirolo amorfo dovrebbe sdoppiarsi nel polistirolo isotattico cristallino in due bande a polarizzazione totalmente perpendicolare o totalmente parallela all'asse dell'elica. Il fatto che sperimentalmente questo sdoppiamento avviene solo in un numero limitato di casi formerà oggetto di un'accurata indagine in un altro lavoro [5].

## 3. – Discussione dei risultati.

È noto che la polarizzazione di una determinata banda può permettere d'individuare la direzione del momento di transizione della vibrazione che l'origina. Nel caso dei polimeri isotattici il comportamento in luce polarizzata deve essere studiato o su campioni orientati amorfi, in modo che non si possa parlare di bande di specie $A$ e di specie $E$ che sono totalmente parallele o perpendicolari, o su campioni orientati cristallini per quelle bande che non risentono dell'interazione di unità monomeriche adiacenti.

I risultati ottenuti in base alle nostre misure hanno permesso di dimostrare essenzialmente corretta l'assegnazione proposta da Liang e Krimm [6] per le bande del polistirolo amorfo ad eccezione dell'attribuzione della fondamentale a 1195 cm$^{-1}$ ad un modo di specie $A_1$ (nel gruppo $C_{2v}$ dei composti benzenici monosostituiti). Infatti in base alle nostre osservazioni (Fig. 7) questa banda presenta una polarizzazione parallela anzichè perpendicolare come richiederebbe la specie proposta. Riteniamo possibile la sua

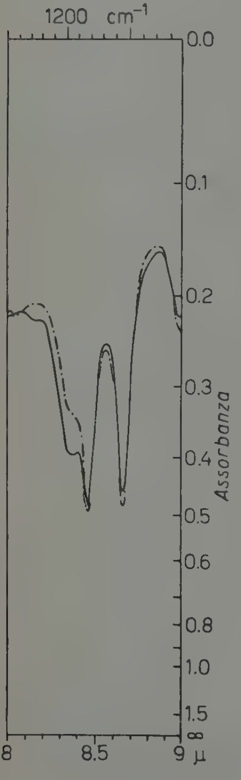

Fig. 7. – Regione a 1195 cm$^{-1}$ dello spettro di un polistirolo atattico stirato. Osservazione in luce polarizzata con vettore elettrico: ——— parallelo alla direzione di stiro; -·-·-· perpendicolare alla direzione di stiro.

assegnazione ad un modo di torsione del gruppo $CH_2$ che presenterebbe la polarizzazione richiesta.

Esaminando le bande d'assorbimento che compaiono nella regione fra 3500 e 1400 $cm^{-1}$ possiamo affermare che la spiralizzazione della catena isotattica del polistirolo in un'elica ternaria non fa comparire nuove bande infrarosse nello spettro del polistirolo isotattico cristallino rispetto ad un polistirolo atattico amorfo orientato se si esclude l'accentuarsi del flesso a 1440 $cm^{-1}$ e la comparsa di una banda molto debole a circa 1980 $cm^{-1}$. Sono invece i rapporti dicroici delle bande che aumentano e si dimostrano in buon accordo con i valori calcolati a priori in base alla struttura cristallina ottenuta con la diffrazione dei raggi X (Fig. 6). Per esempio le bande a 3030 e 3065 $cm^{-1}$, che sono assegnabili a modi normali approssimati di specie $A_1$ del nucleo benzenico monosostituito e comportano quindi una variazione di momento dipolare lungo la congiungente l'atomo di carbonio della catena e quello del nucleo benzenico ad esso legato, presentano una polarizzazione prevalentemente perpendicolare in accordo con il rapporto dicroico calcolato con la nota formula (7)

$$R = \frac{D_z}{D_y} = \frac{2 \cos^2 \Phi}{\sin^2 \Phi},$$

per un valore dell'angolo fra l'asse dell'elica e la congiungente sopra citata di 70° 32′. Abbiamo potuto applicare questa formula anche per il polistirolo isotattico cristallino orientato in quanto l'evidenza sperimentale indicava che per le due frequenze considerate non si verificavano interazioni fra le vibrazioni di unità monomeriche adiacenti.

Con gli stessi criteri sono stati studiati i rapporti dicroici per le altre bande di specie $A_1$ (nel gruppo $C_{2v}$ dei composti benzenici monosostituiti) a frequenze superiori a 1400 $cm^{-1}$ e l'accordo qualitativo fra previsione teorica e dati sperimentali è stato sempre osservato.

Le bande di specie $B_1$, che comportano una variazione del momento dipolare sempre nel piano del nucleo benzenico, ma normale a quella delle bande di specie $A_1$, presentano sperimentalmente una polarizzazione perpendicolare pure in accordo con il modello geometrico fissato in base ai dati della diffrazione dei raggi X.

Per le bande del polistirolo isotattico cristallino aventi frequenze superiori a 1400 $cm^{-1}$ l'interpretazione quantitativa del dicroismo secondo il lavoro di Beer [7] non è possibile per la mancanza in questa regione di bande di specie $B_2$ che hanno tutte frequenze più basse.

Le differenze fra gli spettri infrarossi del polistirolo isotattico cristallino e dell'atattico a frequenze inferiori a 1400 $cm^{-1}$ sono state da noi interpretate nel modo seguente. La banda perpendicolare a 1387 $cm^{-1}$ è stata assegnata ad una vibrazione di deformazione dei gruppi CH della catena e quella parallela a 1298 cm⁻¹ ad una vibrazione di wagging dei gruppi $CH_2$. La banda a 1302 cm⁻¹ avente polarizzazione parallela e quella a 1260 cm⁻¹ quasi totalmente perpendicolare, che sembrano provenire entrambe essenzialmente da vibrazioni dell'elica, non vengono qui considerate dettagliatamente in quanto questo problema verrà trattato in seguito in un altro lavoro [5]. Per la terna di bande che il polistirolo isotattico cristallino presenta a 1195, 1189 e 1179 cm⁻¹, le prime due a polarizzazione parallela e la terza perpendicolare, si conferma l'assegnazione della banda a 1179 cm⁻¹ ad una combinazione $\nu_5 + \nu_{16B}$ [6], attribuendo invece la banda a 1194 cm⁻¹ ad una vibrazione di torsione dei gruppi $CH_2$ della catena. Nessuna particolare ipotesi viene qui formulata circa la vibrazione che origina la banda a 1189 cm⁻¹ caratteristica del prodotto cristallino.

Di notevole importanza è la regione intorno a 1070 cm⁻¹ dove compaiono, come si è già detto nella parte sperimentale, le differenze fra il polistirolo isotattico amorfo e l'atattico. La banda unica presente a 1070 cm⁻¹ nel prodotto atattico è stata assegnata da LIANG e KRIMM [6] ad una vibrazione di stiramento del legame carbonio-carbonio della catena ($\nu$ CC) e ad una vibrazione di deformazione dei gruppi CH dei nuclei benzenici $\nu'_{18B}(B_1)$. Essa si sdoppia in modo non molto netto nell'amorfo isotattico e la separazione del doppietto aumenta con il procedere della cristallizzazione del campione. Una spiegazione di questo comportamento si può avere ammettendo per esempio che la perfetta spiralizzazione della catena renda possibile un fenomeno di risonanza fra un modo normale di catena di specie $E$ [5] e il modo del benzene monosostituito $\nu'_{18B}(B_1)$ preesistente nell'amorfo. Si spiegherebbe così anche il fatto che entrambe le bande del doppietto hanno la stessa specie di simmetria, come si vede dalla loro polarizzazione quasi totalmente perpendicolare.

Un'altra banda del polistirolo isotattico amorfo che si sdoppia in due componenti a seguito della cristallizzazione è quella a 983 cm⁻¹. Lo sdoppiamento fa comparire due bande a 984 e 981 cm⁻¹ a polarizzazione perpendicolare e parallela rispettivamente, ma la spiegazione del fenomeno in questo caso è a nostro avviso diversa da quella sopra invocata. Le due bande hanno origine dall'interazione dello stesso modo normale $\nu_5(B_2)$ o $\nu_{10B} + \nu_{16B}$ secondo LIANG e KRIMM [6] nelle unità monomeriche adiacenti entro il periodo d'identità secondo le due specie di simmetria $A$ e $E$ del gruppo di punti $C_3$, come già si è detto nel paragrafo riguardante la previsione teorica dello spettro del polistirolo isotattico. La separazione delle due componenti del doppietto è molto piccola e non si nota nello spettro del polistirolo isotattico cristallino osservato in luce non polarizzata nel quale compare un'unica banda a 983 cm⁻¹ che si intensifica a seguito della cristallizzazione.

Un fenomeno analogo, ma molto più vistoso poichè la separazione del doppietto è di circa 23 cm⁻¹, si nota per la banda che il polistirolo amorfo possiede a 907 cm⁻¹. Anche in questo caso al procedere della spiralizzazione risulta possibile al modo normale approssimato $\nu_{17B}(B_2)$ di una certa unità monomerica di interagire con lo stesso modo normale di un'unità adiacente secondo la specie *A* oppure *E* dando origine così alle due bande altamente polarizzate che cadono a 920 e 897 cm$^{-1}$. La correttezza di quest'interpretazione circa la provenienza del doppietto sopra accennato dalla stessa banda a 907 cm$^{-1}$ è provata anche dalla diminuzione dell'intensità di questa banda al progredire della cristallizzazione e all'intensificarsi delle bande a 920 e 897 cm$^{-1}$. Sembra quindi logico attribuire alla parte amorfa del campione l'assorbimento a 907 cm$^{-1}$ e alla parte cristallina gli altri due. Riteniamo utile ripetere ancora una volta come per la presenza di queste ultime due bande sia sufficiente la perfetta spiralizzazione dalla catena (che noi abbiamo chiamato cristallinità infrarossa) e non sia quindi richiesto l'ulteriore impacchettamento delle diverse catene in un reticolo tridimensionale (cristallinità ai raggi X).

Nella Fig. 8 abbiamo riportato un tentativo di risoluzione grafica delle tre bande sopra considerate in luce polarizzata con il vettore elettrico perpendicolare e rispettivamente parallelo alla direzione di stiramento del campione orientato. Accettando l'ipotesi che venga conservato per la parte amorfa e per quella cristallina (e quindi per tutte e tre le bande) lo stesso coefficiente d'assorbimento possiamo pensare di determinare in base al rapporto fra le aree delle bande a 920 e 897 cm$^{-1}$ e quella della banda a 907 cm$^{-1}$ la percentuale di catene perfettamente spiralizzate presenti in un campione di polistirolo isotattico cristallino orientato. Naturalmente l'accuratezza delle misure è fortemente limitata dall'ipotesi sopra ammessa e dalle difficoltà pratiche inerenti alla risoluzione grafica delle tre bande sovrapponentesi. Poichè anche la preparazione

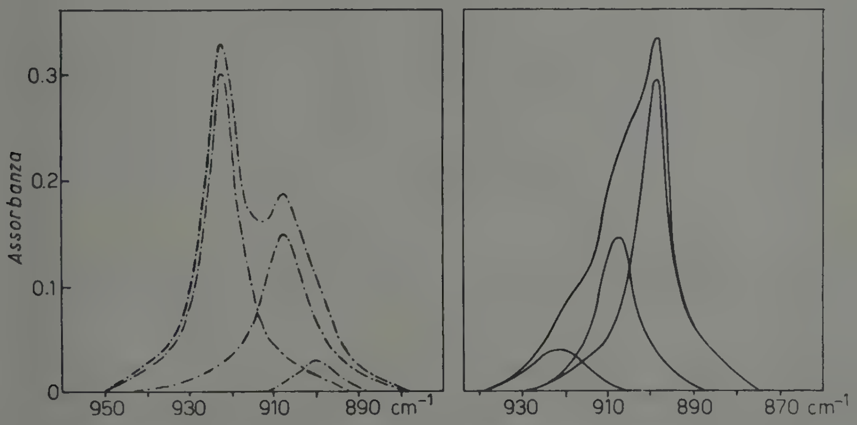

Fig. 8. – Risoluzione grafica del tripletto di bande a circa 900 cm$^{-1}$ in un polistirolo isotattico cristallino. Osservazione in luce polarizzata con il vettore elettrico: —— parallelo alla direzione di stiro; -·-·-· perpendicolare alla direzione di stiro.

di un campione del tipo di quelli necessari per l'effettuazione di queste misure può richiedere molto tempo, abbiamo preferito in generale valutare la percentuale di cristallinità infrarossa di un campione riferendoci la confronto dell'assorbanza della banda a 983 $cm^{-1}$ con quella della banda a 965 $cm^{-1}$. Quest'ultima non è influenzata dalla cristallizzazione mentre la prima s'intensifica in misura molto notevole come risulta dalla Fig. 4.

La banda di polarizzazione totalmente parallela a 784 $cm^{-1}$ è completamente assente nel polistirolo atattico ed isotattico amorfo e compare nello spettro dei prodotti cristallini; essa è probabilmente attribuibile ad un modo di catena di specie $A$.

Nella Tabella I le bande che compaiono nello spettro a seguito della cristalizzazione del campione, tranne la deformazione $\delta$(CH) e la banda attribuita alla vibrazione di wagging $\gamma_w(CH_2)$, sono state attribuite a specie di simmetria nel gruppo di punti $C_3$, in quanto solo esse provengono dall'interazione di unità monomeriche adiacenti e perciò la loro polarizzazione che è quasi totale descrive il comportamento rispetto alle operazioni di simmetria del periodo d'identità nel suo insieme. Per le bande presenti nell'amorfo la polarizzazione non indica l'assegnazione ad una particolare specie, in quanto, essendo le unità adiacenti debolmente accoppiate, il rapporto dicroico è fissato soltanto dalla posizione geometrica del gruppo che per vibrazione origina la banda.

## 4. – Conclusioni.

L'esame infrarosso del polistirolo isotattico ha permesso di stabilire alcuni punti molto importanti e cioè:

1) Esiste una quasi completa identità fra gli spettri del prodotto isotattico amorfo ed atattico, le minime differenze rilevate essendo da ritenere legate alla permanenza in corti tratti di catene di strutture uguali a quelle presenti nei prodotti cristallini.

2) Il fenomeno della cristallizzazione di un campione quale si manifesta nello spettro infrarosso di macromolecole a configurazione elicoidale è legato alla spiralizzazione delle catene e fa comparire numerose bande d'assorbimento atte alla caratterizzazione di un prodotto cristallino.

3) Nei polimeri isotattici cristallini, a differenza dei polimeri non cristallini, non è più possibile considerare debolmente accoppiate tutte le vibrazioni di unità monomeriche adiacenti.

4) In base ai risultati finora acquisiti sembra lecito, nella previsione dello spettro infrarosso di macromolecole elicoidali di poliidrocarburi, prescindere dall'influenza dell'impacchettamento del reticolo cristallino.

Restano aperti numerosi altri problemi, ad esempio quello relativo all'orientamento dei nuclei benzenici del polistirolo allo stato amorfo. Ad alcuni di essi dedicheremo attenzione nelle note successive riguardanti alcuni polistiroli sostituiti nel nucleo aromatico.

* * *

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# Spettri infrarossi di polibutadieni.

## I. - Polibutadiene-1,2 sindiotattico.

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(ricevuto il 26 Giugno 1959)

Il presente lavoro è il primo di una serie intesa a studiare, mediante l'esame degli spettri infrarossi e l'applicazione della teoria dei gruppi, i diversi polimeri cristallini del butadiene-1,3 ottenuti per la prima volta nel nostro Istituto.

Presupposto di questo studio è la conoscenza almeno parziale della struttura delle macromolecole esaminate, conoscenza già acquisita, in base ai dati di diffrazione dei raggi X, per il polibutadiene-1,2 sindiotattico, 1,2 isotattico e 1,4-cis, mentre non è ancora completamente determinata la struttura del polibutadiene a concatenamento 1,4-trans.

Il primo polimero che prendiamo in esame è il polibutadiene-1,2 sindiotattico che possiede un concatenamento testa-coda 1,2 delle unità monomeriche e differisce strutturalmente da un'altro tipo di polimero pure con concatenamento 1,2, il polibutadiene-1,2 isotattico, che sarà oggetto di uno studio ulteriore.

## 1. – Parte sperimentale.

1·1. *Apparecchiatura usata.* – L'esame dello spettro infrarosso dei polimeri studiati, limitato per ora alla zona $2 \div 15$ μm, è stato effettuato con uno spettrofotometro Perkin-Elmer Modello 21 fornito di ottica di cloruro sodico. Le osservazioni in luce polarizzata sono state condotte con polarizzatori a lamine di cloruro d'argento. La cella che è servita per l'esame del polimero fuso è analoga a quella descritta in letteratura da Richards e Thompson [1].

1·2. *Preparazione dei campioni.* – Il polibutadiene-1,2 sindiotattico è stato preparato usando come catalizzatore alluminio trietile-triacetilacetonato di vanadio secondo il procedimento descritto da G. Natta e uno di noi in un recente brevetto [2]. L'esame spettroscopico infrarosso è stato effettuato sulla frazione del polimero solubile a freddo in benzolo, in quanto questa frazione è risultata ad altissimo tenore in concatenamento 1,2 all'esame infrarosso, cristallina all'esame roentgenografico, facilmente purificabile e manipolabile.

I vari campioni sono stati esaminati sotto forma di pellicole aventi spessore di qualche centesimo di millimetro ottenute generalmente evaporando in atmosfera inerte soluzioni del polimero in solventi basso bollenti ($CS_2$, $CCl_4$) su lamine di cloruro sodico mantenute poi sotto vuoto spinto fino alla completa eliminazione del solvente. Talvolta, per l'ottenimento di film di spessori più elevati, si è fatto ricorso allo stampaggio tra piastre di metallo portate a circa 160° C temperatura prossima a quella di fusione del polimero. Lo stampaggio è stato effettuato molto rapidamente per evitare sensibili alterazioni di carattere ossidativo, la cui assenza nei campioni utilizzati è stata riconosciuta in base alla mancanza di assorbimenti nelle regioni di circa 3 400 e 1 700 $cm^{-1}$.

L'orientamento dei campioni per l'esame in luce polarizzata è stato ottenuto per stiramento a freddo di lamine stampate ed è riuscito bene per tutti i prodotti non alterati da reticolazione.

1·3. *Risultati ottenuti.* – La Fig. 1 presenta lo spettro infrarosso di un campione di polibutadiene-1,2 sindiotattico allo stato solido nella regione fra 2 e 15 micron e quello di una soluzione di polimero in solfuro di carbonio nella regione fra 7,3 e 13,4 micron. Nella Fig. 2 è riportato invece lo spettro infrarosso

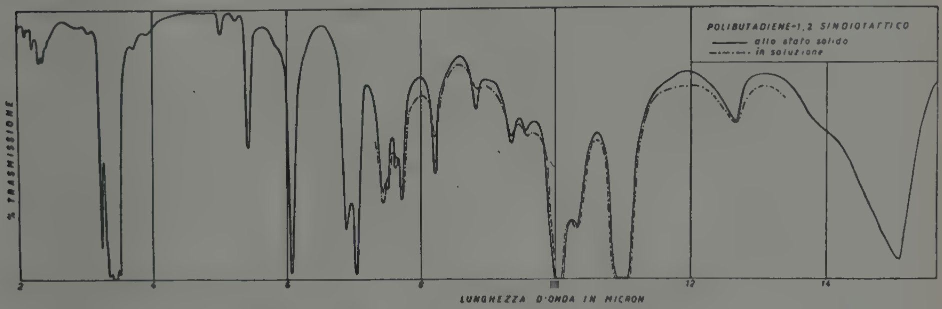


Fig. 1. – Spettro infrarosso del polibutadiene-1,2 sindiotattico.

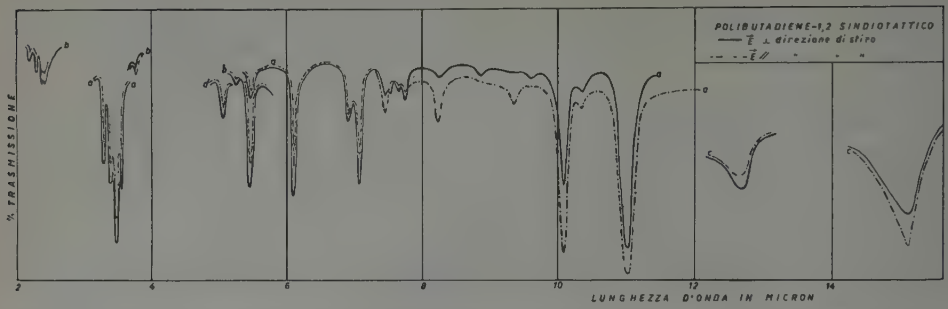


Fig. 2. - Spettro infrarosso del polibutadiene-1,2 sindiotattico in luce polarizzata con il vettore elettrico: –·–·–·– parallelo alla direzione di stiro; ——— perpendicolare alla direzione di stiro (*a*, *b*, *c*, *d* indicano spessori crescenti del film).

di un campione orientato osservato in luce polarizzata con il vettore elettrico alternativamente parallelo e perpendicolare alla direzione di stiramento.

## 2. – Assegnazione delle bande di assorbimento nell'infrarosso.

Lo studio della diffrazione dei raggi X effettuato da NATTA e CORRADINI [3] ha chiarito l'appartenenza del polibutadiene-1,2 sindiotattico al gruppo spaziale Pacm, con quattro molecole di monomero appartenenti a due diverse catene macromolecolari nella cella elementare.

Nella nostra trattazione ci siamo limitati all'analisi vibrazionale di una singola macromolecola, ma questo non costituisce a nostro giudizio una limitazione troppo seria poichè l'entità delle interazioni fra molecole adiacenti non dovrebbe essere molto sensibile dato il tipo di impacchettamento proposto [3]. Ricordiamo inoltre che i risultati ottenuti da LIANG, KRIMM e SUTHERLAND [4] su altri polimeri permettono di affermare che le caratteristiche essenziali dello spettro infrarosso di un polimero cristallino possono essere ottenute dalla considerazione di una singola macromolecola. Lo studio della cella unitaria nel suo insieme può in generale portare a differenze di due tipi: piccole variazioni del valore e talora sdoppiamento in più componenti di certe frequenze fondamentali e modificazione delle regole di selezione per effetto della mutata simmetria.

Considerando una singola macromolecola il periodo di identità di 5.1 Å lungo l'asse della catena corrisponde a due unità monomeriche di butadiene polimerizzato in 1,2. Dei quattro atomi di carbonio facenti parte della catena due portano i gruppi vinilici e sono asimmetrici e alternati con opposta configurazione (*D* e *L* rispettivamente). La Fig. 3 riporta l'unità sterica fondamentale in una molecola singola infinitamente lunga di polibutadiene-1,2 sindiotattico. Da essa si rileva che lo scheletro costituito dagli atomi di carbonio indicati con 1, 2, 3 e 4 non è planare poichè le proiezioni dei legami C-C su un piano perpendicolare all'asse della catena formano un angolo di alcuni gradi. Noi abbiamo però introdotto nella nostra trattazione un'ulteriore semplificazione supponendo planare lo zig-zag degli atomi di carbonio della catena in quanto abbiamo considerato quest'ipotesi non pregiudizievole per i nostri scopi consistenti nella previsione del carattere dicroico delle bande che ci servirà di guida nella loro assegnazione.

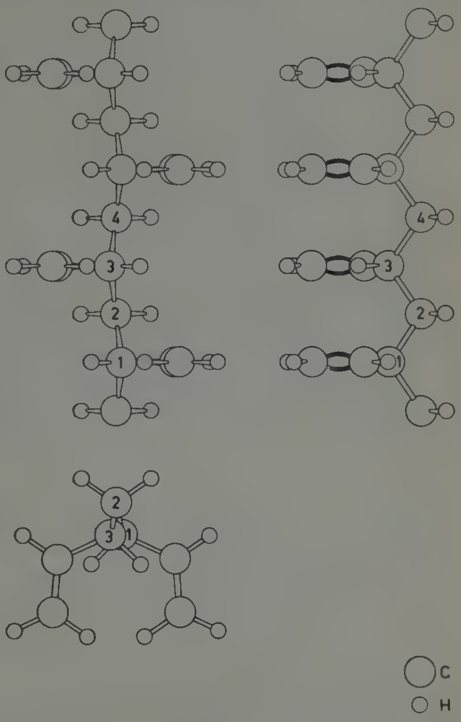
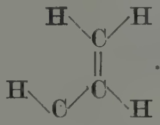


Fig. 3. – Modello della catena del polibutadiene-1,2 sindiotattico.

Nelle ipotesi sopra enunciate le operazioni di ricoprimento permesse sono le seguenti (vedere Fig. 4):

*a*) Riflessione su due piani equivalenti perpendicolari all'asse della catena, piani contenenti ciascuno un gruppo . Con riferimento al piano *yz* di una terna cartesiana li indicheremo con $\sigma_v(y, z)$.

*b*) Riflessione seguita da una traslazione di $c/2$ (dove $c$ è il periodo d'identità lungo l'asse della catena) su un piano contenente lo zig-zag degli atomi di carbonio. Con riferimento al piano *xz* della terna cartesiana indicheremo questo piano con $\sigma_{vg}(x, z)$.

*c*) Rotazione intorno a due assi di simmetria equivalenti, perpendicolari all'asse della catena (asse *x*) e contenuti nel piano $\sigma_{vg}(x, z)$, assi che bisecano l'angolo formato dai legami C—H dei gruppi $CH_2$. Tali assi verranno indicati con $C_2(z)$.

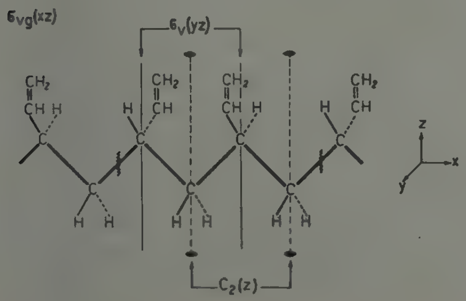


Fig. 4. – Parte di una catena di polibutadiene-1,2 sindiotattico e relativi elementi di simmetria.

L'esistenza di questi elementi di simmetria permette di concludere che il « line group » della catena possiede un « factor group » isomorfo col gruppo di punti $C_{2v}$, mediante il quale lo spettro infrarosso può essere analizzato [5].

Poichè l'unità sterica fondamentale corrispondente al periodo d'identità consta di due unità monomeriche e perciò di 20 atomi, dovremo attenderci $(3 \times 20) - 4 = 56$ modi normali genuini complessivi, in quanto sono ancora genuine le rotazioni intorno alla coppia di assi perpendicolari all'asse della catena.

Per semplificare l'analisi vibrazionale, abbiamo suddiviso, secondo BAGHAVANTAM [5], i modi normali in modi interni e modi esterni, separando idealmente entro l'unità sterica fondamentale sei frammenti: due gruppi $CH_2$, due CH, due $CH = CH_2$.

La Tabella I fornisce il carattere delle varie specie di simmetria per le operazioni del gruppo $C_{2v}$, il numero di modi normali di ciascuna specie ($n_i$) e la loro distribuzione fra traslazioni pure ($T$), vibrazioni di tipo traslatorio ($T'$), vibrazioni di tipo rotatorio ($R'$) e modi normali interni ($n_i'$), insieme con la polarizzazione e le regole di selezione per l'attività Raman e infrarossa delle singole specie.

TABELLA I. – *Specie di simmetria, numero dei modi normali e regole di selezione per una macromolecola isolata di polibutadiene-1,2 sindiotattico.*

| $C_{2v}$ | $E$ | $C_2(z)$ | $\sigma_v(xz)$ | $\sigma_v(yz)$ | $n_i$ | $T$ | $T'$ | $R'$ | $n_i'$ | infrarosso | Raman | Polarizzazione |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | 18 | 1 | 4 | 3 | 10 | *a* | *a* | $T_z(\sigma)$ |
| $A_2$ | 1 | 1 | −1 | −1 | 11 | 0 | 3 | 5 | 3 | *ia* | *a* | — |
| $B_1$ | 1 | −1 | 1 | −1 | 12 | 1 | 3 | 6 | 2 | *a* | *a* | $T_x(\pi)$ |
| $B_2$ | 1 | −1 | −1 | 1 | 19 | 1 | 5 | 4 | 9 | *a* | *a* | $T_y(\sigma)$ |

| | |
|---|---|
| $n_i$ | vibrazioni normali complessive (interne + esterne + non genuine) |
| $T$ | traslazioni pure |
| $T'$ | vibrazioni esterne di tipo traslatorio |
| $R'$ | vibrazioni esterne di tipo rotatorio |
| $n_i'$ | vibrazioni interne |
| *a* | attiva |
| *ia* | inattiva |
| ... ($\sigma$) | perpendicolare |
| ... ($\pi$) | parallela |

La Tabella II fornisce invece le specie di simmetria, le regole di selezione infrarosse e Raman e la polarizzazione delle prime armoniche e delle bande di combinazione [6].

La polarizzazione, o comportamento in luce polarizzata, di una banda infrarossa (fondamentale, armonica o di combinazione) di una determinata specie di simmetria è stata determinata considerando la traslazione appartenente a quella specie. Le bande di specie $A_1$ e $B_2$ hanno quindi una polarizzazione perpendicolare all'asse della catena, mentre le bande di specie $B_1$ mostrano una polarizzazione parallela (vedi Tabella I e II).

TABELLA II. – *Specie di simmetria, regole di selezione e polarizzazione per le bande armoniche e di combinazione per il gruppo di punti $C_{2v}$.*

| | |
|---|---|
| $A_1(\sigma) \times A_1(\sigma) = A_1(\sigma)$ | $A_1(\sigma) \times B_1(\pi) = B_1(\pi)$ |
| $A_2(ia) \times A_2(ia) = A_1(\sigma)$ | $A_1(\sigma) \times B_2(\sigma) = B_2(\sigma)$ |
| $B_1(\pi) \times B_1(\pi) = A_1(\sigma)$ | $A_2(ia) \times B_1(\pi) = B_2(\sigma)$ |
| $B_2(\sigma) \times B_2(\sigma) = A_1(\sigma)$ | $A_2(ia) \times B_2(\sigma) = B_1(\pi)$ |
| $A_1(\sigma) \times A_2(ia) = A_2(ia)$ | $B_1(\pi) \times B_2(\sigma) = A_2(ia)$ |

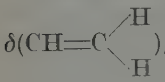
Inoltre, valendoci dei risultati noti dallo studio di molecole piccole, ci siamo costruiti i modi normali « approssimati » combinando le vibrazioni interne ben note dei singoli gruppi chimicamente uguali entro l'unità sterica fondamentale. Questi gruppi, per la particolare struttura sindiotattica del polibutadiene-1,2 in esame, possono avere uno sfasamento nel moto di 0 oppure di $\pi$. Questi modi approssimati permettono quindi una descrizione fisica del moto, pur lasciando imprecisata l'ampiezza delle vibrazioni [7].

2·1. *Modi normali di specie $A_1$.* – Presentano polarizzazione perpendicolare e sono attivi in infrarosso e nell'effetto Raman. La banda a 2980 cm$^{-1}$ viene da noi attribuita allo stiramento simmetrico dei legami $=\underset{|}{\mathrm{C}}-\mathrm{H}$ adiacenti al doppio legame, quando i due gruppi vinilici si trovano durante la vibrazione in accordo di fase. Questa vibrazione verrà indicata con $\nu_s\,(\mathrm{CH{=}CH_2})_i$ dove l'indice $i(=$ in fase) specifica appunto l'accordo di fase tra il moto di una unità ideale e quello dell'unità ideale adiacente. Nell'etilene si trova a 2990 cm$^{-1}$ una vibrazione analoga, contrassegnata con $\nu_{11}$ nella notazione di HERZBERG [8]; nell'intorno di questa posizione si trovano pure gli assorbimenti di tutti gli etileni monosostituiti [9]. L'appartenenza del modo normale $\nu_s\,(\mathrm{CH=CH_2})_i$ alla specie $A_1$ anzichè alla specie $B_2$, la quale presenta pure un dicroismo perpendicolare, si determina esaminando il comportamento rispetto alle operazioni del gruppo $C_{2v}$ del modo $\nu_{11}$ dell'etilene. Un'approssimazione di questo genere si dimostra valida in numerosi altri casi [10], mentre le eccezioni sono da attendersi a frequenze più basse e sono da interpretarsi come una partecipazione degli atomi di carbonio della catena al modo normale approssimato che si considera (nostri lavori in preparazione). La banda a 2847 cm$^{-1}$ è univocamente attribuita allo stiramento simmetrico dei legami CH dei gruppi metilenici e precisamente al modo normale approssimato in cui i due gruppi metilenici vibrano in fase $\nu_s(\mathrm{CH_2})_i$: Le frequenze di questo tipo sono state dettagliatamente studiate [11] negli idrocarburi saturi, e nel politene, per i quali viene riportato un valore di circa 2853 cm$^{-1}$.

La terna di bande tra 2000 e 1800 cm$^{-1}$, presente in tutti i composti contenenti gruppi vinilici [12], è stata assegnata come segue: la banda a 1989 cm$^{-1}$ all'armonica della banda di specie $B_1$ a 991 cm$^{-1}$ ($2\times991 = 1982$; $B_1\times B_1 = A_1$); la banda a 1910 cm$^{-1}$ alla combinazione delle bande a 991 e 908 cm$^{-1}$ ($991 + 908 = 1899$; $B_1\times B_1 = A_1$); la terza banda a 1835 cm$^{-1}$ all'armonica della banda a 908 cm$^{-1}$ ($2\times908 = 1816$; $B_1\times B_1 = A_1$).

L'intenso assorbimento a 1643 cm$^{-1}$ proviene invece dallo stiramento del doppio legame C=C etilenico dei gruppi vinilici; il modo normale corrispondente viene attribuito data la notevole intensità alla vibrazione in fase $\nu(\mathrm{C{=}C})$ [13].

A 1452 cm$^{-1}$ cade la banda proveniente dalla vibrazione di deformazione angolare dei gruppi metilenici attribuita al modo $\delta(\mathrm{CH_2})_i$ [4].

La banda a 1419 cm$^{-1}$, corrispondente alla $\nu_{12}$ dell'etilene [8, 9] è la  $\delta\left(\mathrm{CH{=}C}\begin{smallmatrix}\diagup \mathrm{H}\\ \diagdown \mathrm{H}\end{smallmatrix}\right)_i$; nel propilene e nel butene-1 [9], la banda corrispondente ha frequenze di 1416 e 1420 cm$^{-1}$ rispettivamente.

2·2 *Modi normali di specie* $A_2$. – Sono inattivi in infrarosso ed attivi nell'effetto Raman. Non essendo stato ottenuto lo spettro Raman del prodotto esaminato, risulta impossibile qualsiasi considerazione.

2·3. *Modi normali di specie* $B_1$. – Sono attivi sia nell'effetto Raman che in infrarosso e presentano una variazione di momento dipolare parallela all'asse della catena. La banda con polarizzazione parallela avente la frequenza più elevata da noi osservata è quella a 2675 cm$^{-1}$ assegnata alla combinazione delle bande a 1419 e 1213 cm$^{-1}$ ($1419 + 1213 = 2632$; $A_1\times B_1 = B_1$). Un'altra banda a 1343 cm$^{-1}$ è presente nella stessa posizione nel solido, nel prodotto fuso e allo stato disciolto e viene da noi attribuita al «wagging» in fase dei gruppi metilenici $\gamma_w(\mathrm{CH_2})_i$ [4]. A frequenza leggermente più bassa (1333 cm$^{-1}$) sul fianco della banda suddetta è presente una banda perpendicolare legata alla cristallinità del polimero, in quanto essa scompare facilmente per fusione. La diversa polarizzazione delle bande a 1343 e 1333 cm$^{-1}$ vieta di supporre che si tratti della stessa vibrazione nel prodotto allo stato amorfo (1343 cm$^{-1}$) e allo stato cristallino (1333 cm$^{-1}$). Inoltre anche in campioni a cristallinità crescente non si verifica una variazione del rapporto delle densità ottiche a favore della banda a frequenza minore. L'origine della banda a 1333 cm$^{-1}$ è quindi probabilmente legata all'interazione tra catene adiacenti, in quanto la considerazione della cella elementare porta ad uno sdoppiamento della $\gamma_w(\mathrm{CH_2})_i$.

Altra banda di specie $B_1$ e di media intensità è quella a 1213 cm$^{-1}$; essa si attenua nel prodotto disciolto e nel fuso, senza però scomparire completamente. Assorbimenti in posizione analoga e con polarizzazione parallela all'asse della catena sono stati da noi osservati nel polibutadiene-1,2 isotattico e nel polibutene isotattico, che presentano analogie di struttura chimica con il composto in esame. In questi due polimeri, che differiscono strutturalmente dal polibutadiene-1,2 sindiotattico per il fatto di possedere un'elica ternaria, si osserva a 1 245 $cm^{-1}$ e rispettivamente a 1 222 $cm^{-1}$ una banda d'intensità paragonabile e di comportamento nei cambiamenti di stato analogo a quello della banda a 1 213 $cm^{-1}$ del nostro prodotto. Quest'ultima viene quindi attribuita a un modo normale approssimato che interessa essenzialmente gli atomi di carbonio della catena del polimero, la $\nu_+(\pi)$ secondo la notazione di KRIMM e coll. [4].

Di specie $B_1$, perchè parallela, è la banda a 1 070 $cm^{-1}$, la cui assegnazione è ancora aperta; anch'essa come la precedente banda di specie $B_1$ a 1 213 $cm^{-1}$ risente in misura notevolissima del passaggio dallo stato cristallino all'amorfo e ha una corrispondente in posizione analoga (1 065 $cm^{-1}$) nel polibutadiene-1,2 isotattico, ma non nel polibutene.

Di indiscussa attribuzione sono le bande parallele a 991 e 908 $cm^{-1}$, che provengono dalla vibrazione di deformazione fuori del piano dei legami $=C-H$ adiacenti ai legami etilenici monosostituiti [9, 12]. Nel propilene queste bande hanno le frequenze 996 e 919 $cm^{-1}$ e nel butene-1 994 e 912 $cm^{-1}$; sono presenti anche nel polibutadiene-1,2 isotattico in posizione pressochè identica. La banda a 991 $cm^{-1}$ viene attribuita a un modo normale approssimato, derivato dal $\nu_4$ dell'etilene (1 027 $cm^{-1}$), che indicheremo come $\gamma_\tau(CH=CH_2)_i$ (per la ragione di questa denominazione si consideri la figura della Tabella III).

TABELLA III. – *Assegnazione delle frequenze infrarosse per il polibutadiene-1,2 sindiotattico.*

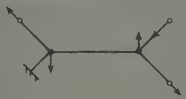
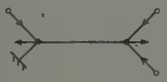
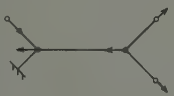
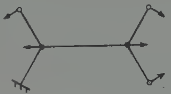
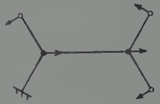
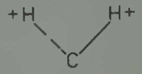
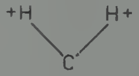
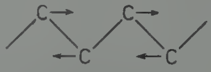
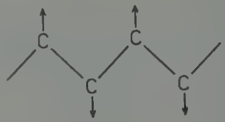
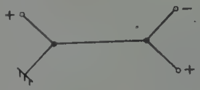
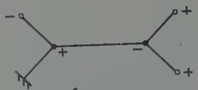
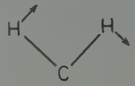
| Frequenza $cm^{-1}$ | Modo normale approssimato | Specie | Polarizzazione | Intensità |
|---|---|---|---|---|
| 3 080 |  $\nu_a(CH=CH_2)_0$ | $B_2$ | $\sigma$ | f |
| 3 012 |  $\nu_s(CH=CH_2)_0$ | $B_2$ | $\sigma$ | fl |
| 2 980 |  $\nu_s(CH=CH_2)_i$ | $A_1$ | $\sigma$ | m |
| 2 913 | $\nu_a(CH_2)_i$ | $B_2$ | $\sigma$ | mf |
| 2 847 | $\nu_s(CH_2)_i$ | $A_1$ | $\sigma$ | m |
| 2 675 | 1 419 + 1 213 = 2 632 | $A_1 \times B_1 = B_1$ | $\pi$ | md |
| 2 550 | — | — | — | fl |
| 1 989 | 2 × 991 = 1 982 | $B_1 \times B_1 = A_1$ | $\sigma$ | d |
| 1 910 | 991 + 908 = 1 899 | $B_1 \times B_1 = A_1$ | $\sigma$ | md |
| 1 835 | 2 × 908 = 1 816 | $B_1 \times B_1 = A_1$ | $\sigma$ | d |

TABELLA III (*continua*).

| Frequenza cm $^{-1}$ | Modo normale approssimato | Specie | Polarizzazione | Intensità |
|---|---|---|---|---|
| 1 643 |  $\nu$ (C=C)$_i$ | $A_1$ | $\sigma$ | f |
| 1 452 | $\delta$ (CH$_2$)$_i$ | $A_1$ | $\sigma$ | m |
| 1 419 |  $\delta$ (CH=CH$_2$)$_i$ | $A_1$ | $\sigma$ | f |
| 1 343 |  $\gamma_w$(CH$_2$)$_i$ | $B_1$ | $\pi$ | m |
| 1 333 | — | — | $\sigma$ | d |
| 1 310 | — | — | $\sigma$ | d |
| 1 294 |  $\gamma_w$(CH$_2$)$_0$ | $B_2$ | $\sigma$ | m |
| 1 265 | — | — | — | fl |
| 1 213 |  $\nu_+(\pi)$ | $B_1$ | $\pi$ | m |
| 1 131 | — | — | $\sigma$ | d |
| 1 070 | — | $B_1$ | $\pi$ | d |
| 1 045 |  $\nu_+$(O) | $B_2$ | $\sigma$ | md |
| 991 |  $\gamma_\tau$(CH=CH$_2$)$_i$ | $B_1$ | $\pi$ | mf |
| 908 |  $\gamma_w$(CH=CH$_2$)$_i$ | $B_1$ | $\pi$ | mf |
| 860 | — | — | — | fl |
| 788 |  $\gamma_r$(CH$_2$)$_i$ | $B_2$ | $\sigma$ | d |
| 770 | — | — | — | fl |
| 664 | — | $B_1$ | $\pi$ | f |

$\nu$ = stretching; $\delta$ = bending; $\gamma_w$ = wagging; $\gamma_r$ = rocking; $\gamma_\tau$ = twisting

s = simmetrico

a = antisimmetrico

i = in fase

o = in opposizione di fase

mf = molto forte

f = forte

m = media

d = debole

md = molto debole

fl = flesso

La banda a 908 $cm^{-1}$ corrisponde al modo normale $\nu_8$ dell'etilene (943 $cm^{-1}$) e l'attribuzione è perciò $\gamma_w(CH{=}CH_2)_i$:

Le due armoniche e la combinazione di queste bande corrispondono, come si è già visto, alla terna di bande tra 2 000 e 1 800 $cm^{-1}$ di specie $A_1$, la cui polarizzazione è in esatto accordo con le previsioni teoriche (vedi Tabella II).

La banda a più bassa frequenza nella regione studiata, avente polarizzazione parallela, è quella a 664 $cm^{-1}$; la sua assegnazione ad una deformazione fuori del piano dei C—H etilenici è fuori dubbio [9], in quanto tutti gli idrocarburi etilenici monosostituiti mostrano assorbimenti in posizioni vicine (per es. il propilene a 578 $cm^{-1}$, l'esene-1 a 632 $cm^{-1}$ e l'eptene-1 a 635 $cm^{-1}$). La forma geometrica del modo normale non può però essere fornita, neppure in prima approssimazione, perchè non esiste la vibrazione equivalente nell'etilene, mentre gli etileni monosostituiti non sono stati ancora adeguatamente studiati.

2·4. *Modi normali di specie* $B_2$. – Attivi sia nell'effetto Raman che in infrarosso presentano polarizzazione perpendicolare. È di specie $B_2$ la banda a 3 080 $cm^{-1}$ che assegnamo allo stiramento asimmetrico dei legami CH dei gruppi vinilici in opposizione di fase $\nu_a$ $(CH{=}CH_2)_0$, il cui modo normale corrispondente nell'etilene ($\nu_5$) cade a 3 075 $cm^{-1}$, mentre propilene e butene-1 hanno assorbimenti rispettivamente a 3 081 e 3 086 $cm^{-1}$. Lo stiramento asimmetrico dei legami CH dei gruppi vinilici in fase $\nu_a(CH{=}CH_2)_i$, pur essendo potenzialmente attivo appartenendo alla specie $A_1$, non possiede un'intensità sufficiente in quanto i due gruppi vinilici vibrano in accordo geometrico di fase, ma la loro configurazione essendo stericamente opposta comporta l'annullamento della variazione di momento dipolare prodotta dalla vibrazione di un gruppo singolo [13].

È pure di specie $B_2$ la banda a 3 012 $cm^{-1}$ attribuita allo stiramento simmetrico dei legami $\overset{}{=}\underset{|}{C}$—H dei gruppi vinilici in opposizione di fase indicato nella Tabella III con $\nu_s(CH{=}CH_2)_0$.

Appartiene alla specie $B_2$ lo stiramento asimmetrico dei legami C—H nei gruppi metilenici $\nu_a(CH_2)_i$ al quale è associabile l'assorbimento a 2 913 $cm^{-1}$, in buon accordo con il valore di 2 923 $cm^{-1}$ trovato per gli idrocarburi saturi.

Alla vibrazione $\gamma_w(CH_2)_0$ attribuiamo l'assorbimento a 1 294 $cm^{-1}$; questa banda è presente anche nei campioni allo stato fuso e per effetto dell'interazione tra catene vicine probabilmente subisce lo sdoppiamento che porta alla comparsa della banda a 1 310 $cm^{-1}$, caratteristica dello stato cristallino.

Ad un modo di specie $B_2$ proponiamo l'assegnazione della banda perpendicolare a 1 045 $cm^{-1}$, in quanto, secondo i calcoli di C. Y. LIANG [4], in tale zona potrebbe trovarsi la banda perpendicolare $\nu_+(0)$, prevista per una catena planare, nel cui periodo di identità siano contenuti quattro gruppi metilenici come si verifica, salvo la sostituzione su atomi di carbonio alterni, anche nei polimeri sindiotattici. Questa banda, come tutte le vibrazioni di catena, si attenua molto nello spettro del prodotto fuso o in soluzione ed è sensibile al variare della cristallinità del campione.

La banda a 788 $cm^{-1}$ cade nell'intervallo caratteristico della vibrazione di « rocking » dei gruppi metilenici e presenta la polarizzazione prevista per un « rocking » in fase dei due gruppi $CH_2$.

2·5. *Altre bande d'assorbimento.* – Oltre alle bande considerate in precedenza, la cui assegnazione a determinate classi di simmetria è possibile, sono stati osservati nella regione (3 400 ÷ 650) $cm^{-1}$ altri assorbimenti la cui origine è legata ad anomalie che si verificano durante la polimerizzazione, o ad alterazioni del prodotto durante la preparazione dei campioni.

Appartengono al primo tipo le bande a 968 $cm^{-1}$ e 735 $cm^{-1}$ dovute a piccolissime quantità (meno del 2 %) di butadiene che durante la polimerizzazione si sono legate con concatenamento 1,4-trans e 1,4-cis rispettivamente.

Provengono invece da alterazione ossidativa del prodotto le bande molto deboli comprese tra 1 700 e 1 680 $cm^{-1}$, nell'intervallo di frequenze caratteristico delle vibrazioni di stiramento dei legami C=O dei gruppi carbonilici.

Non è stata individuata l'origine dei flessi a 2 450 $cm^{-1}$, 1 265 $cm^{-1}$ e 860 $cm^{-1}$ e non è suscettibile di assegnazione la banda a 1 131 $cm^{-1}$, la cui polarizzazione è debolmente perpendicolare.

## 3. – Conclusioni.

Lo spettro infrarosso del polibutadiene-1,2 sindiotattico può essere interpretato considerando che la sua catena possegga un « factor group » isomorfo col gruppo di punti $C_{2v}$. L'esame allo stato disciolto e fuso permette di affermare che le bande più sensibili al passaggio di stato corrispondono a vibrazioni che interessano essenzialmente gli atomi di carbonio della catena o a vibrazioni dovute all'interazione tra catene adiacenti. Queste bande, che presentano un netto dicroismo all'esame in luce polarizzata, possono essere utili per una determinazione quantitativa della cristallinità del polimero, qualora vengano confrontate con bande dovute a vibrazioni interne dei singoli gruppi funzionali.

* * *

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